# Final Report Addendum

## Characterization of Contaminant Migration Potential Through In-Place Sediment Caps

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# I. Executive summary

By isolating contaminated sediments, capping can effectively reduce exposure to contaminants and the potential for contaminant transport into the food chain. However, typical sand caps have little sorption capacity to retard the transport of hydrophobic contaminants such as PAHs that can be mobilized by groundwater flow. The primary objective of this research was to develop and improve engineering tools for more efficient cap designs by enhancing the scientific understanding of organic contaminant transport through sediment caps and the role of sorbent amendments in enhancing cap performance. Laboratory column experiments were performed using contaminated sediments and capping materials obtained from a creosote contaminated EPA Superfund site. The study examined activated carbon and peat moss amendments to the cap as ways to enhance contaminant retardation.

Laboratory column experiments demonstrated rapid breakthrough of lower molecular weight PAHs in experimental columns when groundwater upflow is simulated through a cap. Within a few bed volumes of flow, all 12 PAHs measured were found to break through the 60 cm of capping material. PAH concentration in the capping material was low and comparable to background levels typically seen in depositional sediment, but the porewater concentrations were high. A key conclusion of this comparison is that measurement of PAH concentration in cores taken out of sediment caps is a poor indicator of contaminant breakthrough, especially in cases where there is little capacity in the cap material to trap contaminants. In-situ porewater concentrations need to be measured to provide an assessment of contaminant movement through caps. Column experiments with a natural organic matter (peat moss) delayed PAH breakthrough in the cap. The most dramatic result was observed for caps amended with activated carbon at a dose of 0.2 and 2% by weight. PAH concentrations in the cap pore water in the activated carbon amended caps were several orders of magnitude lower than concentrations in the porewater in the source sediments even after several hundred bed volumes of flow. Thus, enhancing the sorption capacity of caps with activated carbon amendment even at a low dose appears to make a major impact on the quality of porewater achieved in the cap. Sediment caps with and without biological activity did not show remarkable difference for the flow conditions tested. However, mathematical simulation of much slower flowrates expected in the field indicated a bigger impact of biodegradation on PAH migration. It is also possible that in the long-term over many years, a biological community in the form of biofilms may develop in the capping material that adds to the effectiveness of the cap. However, this could not be observed in the short-term (several months) of laboratory experiments.

It is critical to note that scientifically appropriate performance criteria needs to be chosen to monitor the performance of a capping remedy. For example, if PAH concentration in the cap is the criteria, an unamended sand cap that allows PAH laden groundwater to flow through and contaminate the overlying surface water may look superior to a carbon amended cap that adsorbs the migrating PAHs and retains the contaminants in the cap keeping the surface water protected. Long-term mathematical simulations demonstrated that even at a very small dose of GAC amendment (0.002%) to a sand cap, breakthrough is delayed to 10 years and with 0.2% AC, the breakthrough is longer than 1000 years. It is possible that mass transfer limitations within carbon particles and fouling of the carbon with other organic molecules may degrade long-term performance to some extent. However, with the large reductions in PAH transport evident from the laboratory experiments and modeling simulations with GACamended sand caps, it appears promising to include GAC amndments in sand caps to enhance performance where groundwater advection is of concern.

# II. Research Objectives

The primary objective of this research was to develop and improve engineering tools for more efficient cap designs by enhancing the scientific understanding of organic contaminant transport through sediment caps. To achieve this objective, the following research questions were addressed:

1. Can pore water movement due to groundwater potential enhance contaminant mobilization and influence long-term effectiveness of sediment caps for the protection of benthic and aquatic environments?
2. Can improved understanding of actual porewater concentrations and contaminant binding in natural or engineered capping materials enhance predictive capability of cap performance and facilitate more effective cap design?
3. Can selection of an appropriate natural capping material and amending the sorptive capacity with sorbents (e.g., activated carbon), ensure long-term contaminant stability and minimize vertical contaminant transport where advective processes are of concern?

These research questions were addressed by performing laboratory measurements of PAH transport processes and mathematical modeling. Laboratory column experiments were performed using contaminated sediments and capping materials obtained from a creosote contaminated EPA Superfund site. The study examined activated carbon and peat moss amendments to the cap as ways to enhance contaminant retardation. The study used innovative laboratory tools, analytical techniques, and numerical modeling to build on the current knowledge of contaminant transport through caps. PAHs are the model contaminants in this study, but findings here for PAHs could be transferred to other hydrophobic organic contaminants.

# III. Background

By isolating contaminated sediments, capping can effectively reduce exposure to contaminants and the potential for contaminant transport into the food chain. One third of the 60 Tier I contaminated sediment sites in the United States involve capping and about 20% of the tier 1 sites involve PAHs (http://www.epa.gov/superfund/health/conmedia/sediment/data.htm). The sources of PAH contamination in sediments are typically from coal and petroleum processing and use. Many contaminated freshwater and marine sediment sites reside in shallow, near shore areas that are often impacted by advective processes (e.g., groundwater flow, tidal pumping, and wave pumping), benthic bioturbation, and hydrodynamic forces. These forces contribute to the flux of contaminants through sediments. Current cap design methods do not adequately account for contaminant transport processes and for organic content and type when selecting capping materials and designing cap thicknesses, despite the known significant impact of organic matter on contaminant sorption and transport. Material selection criteria are based primarily on cap stability considerations (Palermo, Clausner et al. 1998), affected largely by surface water hydrodynamic forces, and most caps are conservatively designed based on a theoretical understanding of contaminant transport.

Current state of art in sediment cap design is documented in the US EPA capping guidance (Palermo, Maynord et. al. 1998) and the US Army Corps of Engineers Capping Guidance Document (Palermo, Clausner et al. 1998). Cap design guidance in these documents focuses on establishing sufficient cap thickness to protect benthic organisms by isolating contaminated sediments beneath a sufficiently thick layer of clean sand. Although the potential for contaminant transport through sediment caps is acknowledged in these design documents, it is not included as a design criterion. The following key features were identified from the guidance documents and from a review of historically placed caps:

- Caps normally are composed of clean sediment (these are commonly referred to as sand caps)
- Contaminant transport in a cap may be predicted using a model that describes contaminant transport through a porous medium
- 1-D models often assume sorption equilibrium, using sorption coefficients calculated from contaminant partition coefficient ($K_d$, measured or estimated from $K_{ow}$)
- Possible use of activated carbon as sand cap amendment is mentioned, but the documents do not include discussions of experimental studies or how such amendments should be designed and placed.

A submerged cap provides physical isolation of the contaminated sediment by preventing re-suspension and distances benthic communities from the pollution source. This remediation method is suited for areas with minimal currents, waves, ship traffic and ice, to allow for long term cap integrity (Palermo, M.R., Clausner. et. al., 1998). It has been shown that capping is effective when diffusive forces are the primary mechanism by which contaminants are transported in the porewater (Murphy, P., et al., 2006; Thoma, G.J., et al., 1993; Eek, E., et al. 2008) Advection during tidal pumping (Simpson, S.L. et al. 2002) and groundwater discharge (Viana, P.Z. et. al. 2008; Burnett, W.C., et al., 2003; Liu, C., et al., 2001; Boehm, A.B. et al. 2004) can adversely affect cap performance. A literature review by Liu et al. (2001) showed that specific discharge rates of submarine flow range from $1.08\times10^{-6}$ to 0.3 m/hr. It is likely that the high discharge rates are during low tide and are not averaged over high and low tide periods. In general, average specific discharge rates greater than $1\times10^{-4}$ m/hr are considered high. At Hood Canal, WA average groundwater discharge rates were measured to be 0.036 m/hr (Swarzenski, P.W, 2007). Groundwater advection could lead to the transport of metals (Viana, P.Z. et al. 2008) and organics such as polycyclic aromatic hydrocarbons (PAHs) (Hyun, S. et al. 2006) and polychlorinated biphenyls (PCBs) (Murphy, P. et al. 2006).

Hydrodynamic, sorptive, and geotechnical conditions within the cap need to be designed to minimize contaminant flux to the surface water (Mohan R.K., et al., 2000; Wright, S.J., et al. 2001). Some capping approaches have tried to minimize contaminant flux by diverting the upwelling groundwater away from the contaminated sediment (Barth E. F., et al., 2008). A sediment cap that is impermeable will do little to minimize long term risk at sites of potential groundwater discharge if contaminated groundwater flows around the cap. At the Wyckoff, Eagle Harbor Superfund site in Washington, groundwater seepage has been observed (averaged 0.001 m/hr in one of two locations measured), and the migration of polycyclic aromatic hydrocarbons (PAHs) may be greatly increased by advective processes in some areas (Magar, V.S. et al. 2007). The site was a wood processing facility and is the source of creosote contamination (http://yosemite.epa.gov/R10/CLEANUP.NSF/sites/Wyckoff). PAHs in the creosote are known to cause a variety of adverse biological effects in marine fish. After capping the site with sediment and sand, indicators of flatfish health (e.g. biliary fluorescent aromatic compounds, hepatic DNA adducts, and lesion risk) have been improving for 11 years (Myers, M.S. et. al. 2008).

**Biological activity in sediment caps.** It has been demonstrated that bacteria can colonize capping material in column experiments (Himmelheber, D.W. et al. 2009). In situations where tidal pumping is

occurring, it is conceivable that oxygen might be carried from the surface to serve as a terminal electron acceptor (TEA). Oxygen and nutrients have the greatest influence on the effectiveness of PAH degradation in sand caps (Hyun, S. et al. 2006). With PAHs of molecular weight greater than pyrene, degradation may be limited even in aerated conditions (Hyun, S. et al. 2006). Within both sediment and cap layers of the columns, bioavailability, and consequently degradation of PAHs will be proportional to the number of aromatic rings and alkyl substitutions (White, H.K., et al. 2005).

In marine environments, sulfate would also be supplied from the surface sea water and serve as a TEA. Research has suggested that sulfate reduction is the most relevant for anaerobic marine sediments (Coats, J.D. et al. 1996; Rothermich, M.M. 2002). In the case of groundwater discharge or upwelling, it would be expected that oxygen concentrations would be limited to levels found in typical groundwater (~0.5 mg/L). Groundwater could supply nitrate for nitrate reduction (Swarzenski, P.W., et al. 2007; McNally, N.L. et al. 1998). The porewater from the capping material at Eagle Harbor measured high nitrate levels (66 mg/L) after being stored for 3 years at 4 degrees C. Groundwater typically has much lower nitrate levels (~1mg/L). Other terminal electron acceptors have been detected in caps, with bacterial community composition correlated to depth, $Fe^{2+}$, and $Mn^{2+}$ concentration gradients in the cap (Himmelheber, D. W., et al. 2009).

Microbially mediated redox conditions could increase the amount of humic acid liberated as dissolved organic matter (DOM) (Kim, H.S. et al. 2005) and could therefore influence PAH transport through columns. Experiments have been performed using peat moss amendments to degrade gasoline and BTEX (benzene, toluene, ethyl-benzene and m-, o-, p-xylenes) compounds under microaerophilic conditions (Yerushalmi, L. et al. 1999). While the most rapid degradation occurs while oxygen is present, studies have shown the anaerobic degradation of some low molecular weight PAHs such as naphthalene and 2-methylnaphthalene can be significant if porewater levels of sulfate are maintained at 14-25mM (Rothermich, M.M., et al. 2002). Porewater concentrations of the Eagle Harbor capping material was measured to be 13mM as shipped (again after being stored in a fridge at 4 degrees C for 3 years). This concentration will decrease if freshwater discharge is occurring.

**Role of sorbents in sediment caps**. Sand caps are permeable, but have little ability to sequester organics (Murphy, P., et al. 2006), and do not provide conditions to form insoluble metal sulfides (Simpson, S.L., et al. 2002). A variety of capping amendments are being explored to increase sequestration of metals and organics in sand caps. Apatite and organoclay have the broadest range of effectiveness for metals (Viana, P.Z. et al. 2008), while activated carbon, coke (Zimmerman et al. 2004;

Murphy, P., et al. 2006), peat (Rasmussen, G. et al. 2002), and organoclays (Viana, P.Z., et al. 2008) are being explored for organics. Major factors controlling sorption of organics include: hydrophobicity of the solute, organic carbon content and surface area of the sorbent. In the literature, peat and peat moss have received much attention as an amendment for creosote wastes (Rassmussen, G. et al. 2002; Yerushalmi, L. et al., 1999).

Peat-sand columns were used to treat creosote wastewater (Rasmussen, G. et al. 2002). They used 0.9% peat moss and achieved 94-100% removal of PAHs (slightly better removal with bioactive columns than abiotic columns). The majority of PAH removal was by sorption; however degradation could extend the life of a barrier, especially if PAHs that bind to the peat are still available for degradation. There was no apparent lag time before degradation started, and anaerobic degradation may also have been occurring in the columns (Rasmussen, G. et al. 2002). The authors suggest a two zone treatment method, where an initial zone would contain sand only and rely on biodegradation for removal, and a second zone containing peat would use sorption to remove any compounds that passed the bioactive zone (Rasmussen, G. et al. 2002). Other studies have demonstrated aerobic naphthalene degradation in sand columns (Warith, M., et al., 1998). Experiments using the solid phase microextraction (SPME) technique could provide a more detailed understanding of the high molecular weight PAHs in biologically active capping material. Column experiments have also been conducted to observe the migration of PAHs from freshwater sediment through Ottawa sand caps under advective conditions (Hyun, S. et al. 2006). Hyun et al. observed rapid breakthrough of PAHs in capping material, but when combined with oxic microbial processes, the flux of PAHs could be greatly reduced. These experiments were relatively short and did not account for sediment PAH dissolution. The addition of carbon amendments to the cap was not investigated.

The presence of an in situ cap shifts the location of depositional organic matter and removes the source of nutrients to the sediment (Himmelheber, D.W., et al. 2007). The lack of nutrients, in addition to anoxic conditions, could slow degradation at the sediment-cap interface (Hyun et al. 2006). Some types of organic additions to the cap could alleviate nutrients as a rate limiting factor. Ideally carbon amendments could slow the advective transfer enough to prevent contamination of the benthic zone pore water and surface water, while natural attenuation processes occur in the sediment and cap (Zimmerman, J.R. et al., 2004). Sorption to different forms of organic carbon has not been incorporated into cap designs. Generally sand has been found to be the easiest material to place as a cap and provides the greatest stability on sloped areas (Palermo , Clausner et al., 1998). Different forms of organic carbon could be used in the cap as an amendment. Equilibrium partitioning to the carbon can be used in modeling

approaches. However, the assumption of equilibrium needs to be examined in the sediment and cap. Particularly in the capping layers if pore water velocities are high and/or if inaccessible micro or macro pores exist in the cap. Standard published equilibrium partitioning values may be inadequate because of non-equilibrium conditions or competition effects between the hundreds of compounds found in the creosote and other non-aqueous phase liquids (NAPLs). Ultimately, a capping model may need to incorporate rate-limiting sorption processes by not assuming linear sorption equilibrium. This approach may provide better results when applied to long term modeling on low sorptive capacity sands with low organic content (Schuth, Ch. and Grothwahl, P. et al. 1994; Deane G., et al. 1999; Ran Y., et al. 2005).

# IV. Materials and Methods

**i) Sediment and column materials.** Sediment and clean capping material (sandy gravel) from a representative portion of the cap where freshwater seepage was found occurring, was collected from the Wyckoff/Eagle Harbor, Washington Superfund site in June 2006 and stored at 4°C. The sediment collection effort was conducted as part of a related SERDP project (ER-1370). A detailed description of the source of the capping material is provided in the final report of the field activity portion of the project: ER-1370 (Sass et al., 2009). The material used in the columns was a sandy-gravel obtained from the existing cap in the field. It is representative of the material at the near/on shore areas where groundwater upwelling is most likely occurring (as determined by measuring pore water conductivity/freshening). The offshore Eagle Harbor cap is made of both Snohomish River dredge material (primary cap placed in 1993) and quarry-run sand placed as a secondary cap closer to shore in 2000. (Lyons et al. 2006, Myers et al. 2008).

The contaminated sediment used in this study was obtained by coring under the cap. There was a clayey (highly contaminated sediment) and a sandy (low contaminated sediment). The clayey sediment was obtained from TR5+20B, TR5+20A, TR5-00A, TR4+20A, and TR4+40A cores. The sandy sediment was obtained from TR4-00B and TR5-00A (see Figure 4-2 in Sass et al., 2009). The sandy and clayey sediment were mixed at a ratio 4:1 and then wet sieved to between 180 and 1700μm to obtain the contaminated source material used in the laboratory experiments. This sieve size was chosen because it was a size range in the fractional analysis of the bulk Eagle Harbor sediment that prevented excessive backpressure in the column experiments. It is important to remember that the purpose of the laboratory column experiments were to observe the generic behavior of PAH transport through capping material obtained from the field. The objective was not to replicate site specific source material and conditions at unique locations within the Eagle Harbor Superfund area.

Coal based granular activated carbon (45-180 μm) was obtained from Calgon Corp. (Pittsburgh, PA). Enriched Canadian sphagnum peat moss was obtained from Miracle-Gro Lawn Products, Inc. (Marysville, OH). The peat moss was ground and sieved to 63-1000 μm before being used as an organic carbon amendment. The peat moss was 30.9 % organic carbon. Total organic carbon (TOC) was measured using hydrochloric acid (HCl) pretreatment to remove inorganic carbon and combustion followed by nondispersive infrared (NDIR) detection of $CO_2$ in a Shimadzu TOC analyzer (Model TOC-5000A/SSM-5000A).

Initial sediment PAH characterization was done for the Eagle Harbor sediment and cap samples. The sediment and cap samples were homogenized and stored under refrigeration after it was received. Two

grab samples were taken and two portions (~2 grams wet weight) were taken for extractions from each grab. Extraction and analysis of sediment/cap material used pesticide-grade organic solvents obtained from Fisher Scientific (Pittsburgh, PA). The 16 EPA priority pollutant PAHs were measured in the sediment samples after ultrasonic extraction (EPA method 3550B) and silica gel cleanup (EPA method 3630C). Calibration standards were used at seven levels ranging from 103 to 31,000 µg/L of total 16 PAHs. Two internal standards, 1-floronaphthalene and p-terhpenyl-$d^{14}$, were added to the GC vials prior to injection. Blanks and mid range calibration standards were run with samples to check background PAH levels and the initial calibration respectively. For PAH distribution by particle size, wet sieving was performed on the Eagle Harbor sediments using standard sieve sizes 63µm (mesh #230), 180µm (mesh #80), and 1.7mm (mesh #12). PAH extractions and analysis were performed for each of these sieved portions. Along with wet sample extraction, dry weights of sediment and cap samples were obtained from a portion (~5 grams wet weight) of each grab after overnight drying at 105 $^{o}$C.

**ii) Solid-Phase Micro Extraction (SPME) for PAH measurements.** Ten parent PAHs were measured by solid phase microextraction (SPME) with gas chromatography mass spectrometry (GC-MS) in selected ion monitoring mode (Hawthorne, S.B., et al. 2005). SPME analysis procedure used commercially available 7 µm diameter PDMS [poly(dimethylsiloxane)] coated fibers from Supelco (Bellefonte, PA). A four point calibration was run using deuterated internal standards: naphthalene-d8, acenaphthylene-d10, flourene-d10, phenanthrene-d10, fluoranthene-d10, pyrene-d10 and chrysene-d12. The fiber was cleaned under a helium stream for 30 minutes at 320°C prior to running a set of samples. The fiber was cleaned for 10 minutes under a helium stream at 320°C between each sample run. Further details on the SPME method can be found in Hawthorne et al., 2005 (also in US EPA Method 8272). To verify the SPME technique used for sediment batch experiments, liquid-liquid extraction with hexane was also performed.

**iii) Batch equilibrium measurements.** For sediment equilibrium tests, a known mass ( ~ 1 g) of sieved sediment (180-1700 µm) was placed into each of six 11.5 ml glass vials with a solution of 0.01 M calcium chloride ($CaCl_2$) and 1000 mg/L sodium azide ($NaN_3$) in deionized water and capped with Teflon-lined caps. Vials were placed flat in a cylindrical container and on a roller for 16 days at 0.75 revolutions per minute (RPM). The equilibrated slurry was centrifuged at 4000 RPM for 6 minutes to produce 9 mL of aqueous supernatant from each sample vial that was transferred to new glass vials. Colloids were removed by flocculation by the addition of 0.25 ml of alum (10%wt) and 2 drops of 1N NaOH.

For capping material equilibrium tests, 3 grams of capping material was placed in 60 ml vials, and then filled with a 1000 mg/L $NaN_3$ solution. Capping material that had been baked in an oven at 70 degrees for four hours and capping material that had been baked at 400 degrees C for 4 hours were each used in the batch experiments making two forms of the capping material to be tested (baking at 400 degrees is assumed to remove labile organic carbon). Incremental amounts of PAH standards in acetone solvent were added to 7 vials for each form of the capping material to make a total of 14 vials. To one vial no PAHs were added to measure any PAHs desorbing from the clean capping material. To other vials with no capping material PAHs were spiked to check for losses to the vial cap and glass side walls. The vials were placed on a roller for 14 days after which time the water phase was measured for PAHs using SPME after alum flocculation.

For the peat moss equilibrium tests, approximately 0.1 grams for peat moss was placed in five 250 ml jars and filled with 1000 mg/L $NaN_3$ solution. Incremental amounts of PAHs were added to these five jars and five additional jars that didn't contain peat moss. Equilibration times were 3 weeks. Sorption to the vial glass and vial cap was assumed to be negligible in the presence of the sorbents.

**iv) PAH Analysis by Gas Chromatography-Mass Spectrometry (GC-MS).** PAH extraction of Eagle Harbor sediments and capping material was carried out using sonication with a hexane/acetone (1:1) mixture (based on EPA method 3550B for extraction). Clean-up on the final extract was carried out using an activated silica gel column as outlined in EPA Method 3630C. A gas chromatograph (Agilent model 6890N) with a 0.25-µm bonded fused silica capillary column (DB-5MS, 60 m x 0.25 mm i.d.) coupled with a mass spectrometer (Agilent model 5973 Network Mass Selective Detector) was used for analysis based on EPA method 8270C for 16 parent PAHs.

An initial ultrasonic extraction with acetone followed by a mixture of hexane/acetone (1:1) was used to extract the creosote from the sieved Eagle Harbor sediment. The mass of the total extractable organics was determined gravimetrically by evaporating the solvent from the extract under a steady air stream (similar to EPA Method 9071A).

**v) Column studies.** Column experiments were conducted in 5 cm diameter glass columns with 6 equally spaced Teflon sampling ports as illustrated in Figure 1. Glass wool separated the sampling ports from the sediment and capping material. Port 1 was positioned at the sediment layer and sampled sediment pore water, ports 2-5 were positioned at the capping layers and port 6 was positioned at the overlying water. The sediment was sieved to 180-1700 µm prior to being used in columns to allow for desired flow rates to occur without creating excessive backpressure. Sieving the sediment decreased the total 16 PAH

concentration from 1162 to 850 μg/g. The sediment was placed in the column from the top using a PVC pipe to prevent pre-contamination of the glass side walls. The flow was maintained at 25±5 mL/hr for specific discharge rates (i.e. Darcy velocity) of approximately 0.015 m/h (which is likely 15 times greater than at Eagle Harbor site) and average pore water velocities of 0.05 m/hr. These conditions provide a Reynolds number of 0.0004 which is well below 0.01 to be considered laminar flow. The flow direction was up through a 14 cm deep sediment layer, a 65 cm capping material layer, and 32 cm of overlying water. The sediment and capping material did not compress and these distances remained constant during the length of the experiment, and porosity was assumed to be constant as a function of depth. Three of the four columns were constructed with amendments in the capping material. All columns were run with the influent water containing 0.01M $CaCl_2$ to mimic the ionic strength of groundwater (this conductivity is about 13 times less than the pore water of the capping material as shipped) and 100 mg/L $NaN_3$ (to inhibit microbial activity) in abiotic columns. Ten parent PAHs were measured in pore water samples by SPME GC-MS as described previously. The five column experiments that were run were as follows:

1. killed control column with no amendment to the capping material.
2. killed column with capping material amended with 2% GAC
3. killed column with capping material amended with 0.2% TOC by the addition of peat.
4. killed column with capping material amended with 0.2% GAC
5. biologically active column with no amendments in the cap.

The percent amendment added is by weight. The amendments were mixed in the capping material prior to addition to the columns. The mass-median diameter (D50) values for the GAC and peat amendment were 110μm and 530μm respectively. The D50 value for capping material was 2.75mm.

The flow through the columns was measured by collecting effluent water in a graduated cylinder. The flow was generally 26ml/hr but may have increased to 30ml/hr at times. As a rule of thumb, when the column diameter to particle diameter ratio is greater than 20, the side wall effects are considered to be negligible. Our columns had a column to particle diameter ratio of 18.5, close to the ratio suggested for no wall effects. Tracer studies conducted in the columns packed with capping material show normal Gaussian shape of the tracer and no indication of significant wall effects. Short circuiting would result in fronting of the Gaussian curve, but this is not visible in the tracer results. If glass side walls were of major significance they would have allowed premature breakthrough in the amended columns. This was not observed either as discussed in the later part of the report.

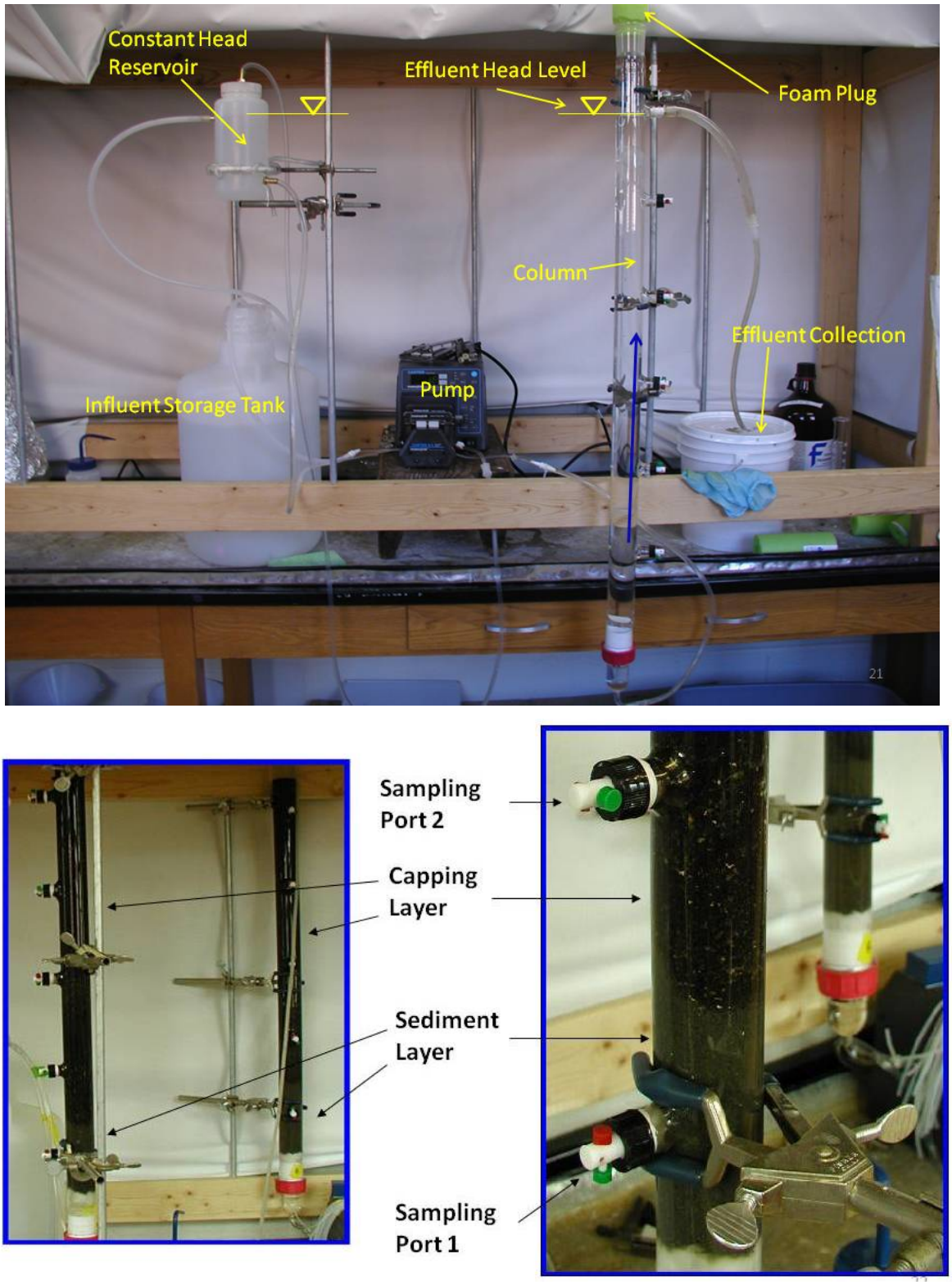


**Figure 1. Pictures of laboratory column setup showing plumbing setup (top) and closeup of sampling ports (bottom)**

**vi) Modeling contaminant transport .** The dissolution of PAHs from multi-component NAPLs (such has creosote) has been modeled previously (Peters, C., et al., 1999). This system more adequately describes the sediment found at many PAH contaminated sites with high concentrations of free phase creosote or coal tar (Hong L. et al., 2003). The modeling utilizes ordinary differential equations describing the mass balances in the creosote and water phases of the modeled porous media. A sediment particle that is coated with a thin layer of creosote can be modeled using Raoult's law and coupled mass balance equations for creosote, aqueous, and solid phases. The mass balance for PAH *i* in the aqueous phase is

$$\frac{dC_i^A}{dt} = k_{ai}\left(C_i^* - C_i^A\right) - \frac{C_i^A}{\tau} - k_{bi}C_i^A \qquad \text{equation 1.}$$

where $C_i^A$ is the concentration of *i* in the aqueous phase (mg/L), $k_{ai}$ is a mass transfer rate constant ($t^{-1}$), $C_i^*$ is the aqueous phase solubility (mg/L), $\tau$ is the aqueous phase residence time (t), and $k_{bi}$ is the biodegradation rate constant, ($t^{-1}$). The solubility is related to creosote composition through Raoult's law

$$C_i^* = X_i^N S_i \qquad \text{equation 2.}$$

where $X_i^N$ is the mole fraction of *i* in the creosote phase, and $S_i$ is the subcooled liquid solubility for *i*. The mass balance for *i* in the creosote phase is

$$W_i \frac{dm_i^C}{dt} = -k_{ai}V^A\left(C_i^* - C_i^A\right) - P_i \qquad \text{equation 3.}$$

where $W_i$ is the molecular weight of *i* (g/mol), $m_i^C$ is the moles of *i* in the creosote phase (mol), $V^A$ is the volume of the aqueous phase ($L^3$), and $P_i$ is the rate of precipitation (or redissolution) of *i*. The mass balance of the solid PAH phase is

$$W_i \frac{dm_i^S}{dt} = P_i \qquad \text{equation 4.}$$

where $m_i^S$ is the moles of solid *i* (mol). Assuming the creosote and solid phases are in equilibrium, solid PAH will begin to form when the PAH's mole fraction reaches its solubility limit in the creosote phase. Solubility limits as well as other properties of PAHs are listed by Peters et al. A conceptual schematic for this model is shown Figure 2.

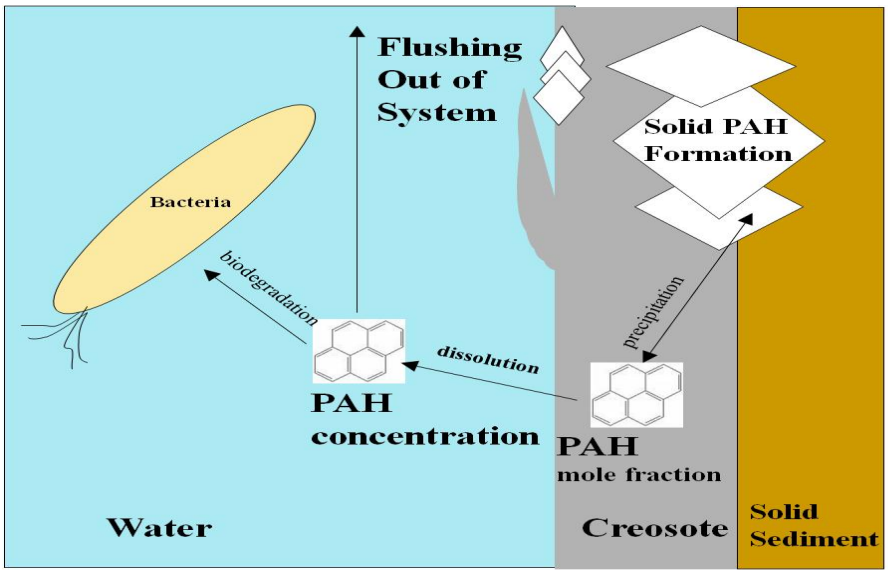


**Figure 2. Conceptual model schematic for PAH dissolution from creosote contaminated sediment.**

Discrepancies in the sediment dissolution model could be explained by the mass transfer rate which assumes homogeneous creosote/water surface area throughout the control volume. In reality, the creosote/water surface area will be least at the inlet end of the column and will increase as the dissolution front is reached (Imhoff, P.T. et al. 1993). The model may fail to describe the creosote/water mass transfer changes if solid PAH formation occurs at the creosote/water interface (Luthy, R.G., et al., 1993; Ortiz, E. et al. 1999). The model assumes equilibrium between the solid and creosote phases. Experimental results of a biologically active column can be compared to the model to see if the mass transfer of PAHs from the sorbed phase to the aqueous phase controls biodegradation rates. Errors in the model could also arise from microbial utilization of sorbed and creosote phase PAHs (Xia, X. et al. 2007).

The migration of a single contaminant in a sediment cap has been described using the one dimensional advection-dispersion equations with retardation for steady state flow in homogenous soil. (Toride et. al. 1999).

$$R\frac{\partial Cr}{\partial t} = D\frac{\partial^2 Cr}{\partial x^2} - v\frac{\partial Cr}{\partial x} - k_B Cr \qquad \text{equation 5.}$$

where $Cr$ is the volume averaged or resident concentration (µg/L) of one particular PAH in the column, $D$ is the dispersion coefficient ($m^2$/day) obtained by tracer studies of capping material columns, $v$ is the average pore-water velocity and $R$ is a retardation factor given by

$$R = 1 + \frac{\rho_b K_d}{n}$$ equation 7.

where $\rho_b$ is the cap solid bulk density (kg/L), $K_d$ is the solid-water distribution coefficient (µg/kg/µg/L), and $n$ is porosity. The distribution coefficient depends on the properties of the capping material and assumes equilibrium partitioning in the cap:

$$K_d = K_d cap + f_{oc} * K_{OC} + f_{ac} * K_{GAC}$$ equation 9.

where $K_{dcap}$ is the solid-water distribution coefficient of non-amended cap, $f$ is the fraction of organic carbon (OC) or granular activated carbon (GAC), $K_{oc}$ and $K_{GAC}$ are the distribution coefficients for OC and GAC respectively. Analytical solutions to the advection-dispersion equation with retardation (Ogata, A. and Banks, R.B., 1961), but without biodegradation, have been utilized for preliminary calculations

$$C = \frac{C_0}{2}\left[ erfc\left( \frac{x - \left(\frac{v}{R}\right)t}{2\sqrt{\left(\frac{D}{R}\right)t}} \right) + \exp\left(\frac{vx}{D}\right) erfc\left( \frac{x + \left(\frac{v}{R}\right)t}{2\sqrt{\left(\frac{D}{R}\right)t}} \right) erfc\left( \frac{x + \left(\frac{v}{R}\right)t}{2\sqrt{\left(\frac{D}{R}\right)t}} \right) \right]$$ equation 10.

where $C$ is the PAH concentration (µg/L) of the column effluent, $C_0$ is the PAH concentration (µg/L) of the column influent, and $x$ is the distance along the column. A numerical simulation (using CXTFIT code) of equation 5 provides the ability to incorporate a changing boundary condition to the cap, biodegradation in the cap, and initial porewater concentrations in the cap.

**vii) Numerical solution for the NAPL dissolution model**

A mathematical model described by the equations presented in the previous section was coded in MATLAB software (where the creosote phase is labeled as non-aqueous phase liquid (NAPL)). A mass transfer coefficient ($days^{-1}$) is used to characterize the migration of PAHs from the creosote phase to the water phase (Imhoff, P.T. et al., 1993). A variable (m_napl_init_total) is set at 0, and is used to calculate the initial amount of moles of PAHs in the system. A variable (m_napl_total) is also set at zero and is used for updating the total amount of moles after each time-step. Arrays are declared for the moles and the mole fraction of PAH *i* in the creosote, the PAH concentration in the aqueous phase, and the solubilities of the PAHs in the creosote. Properties pertaining to each PAH were imported from an excel

file as initializers. The initializers used were as follows: the PAH name, molecular weight, biodegradation rate, initial mole fraction, subcooled liquid solubility, and initial moles. A time array is used to fill out where the initial element is, (initial time) and ends at the maximum number of time points incrementing by the given time step (*dt*) in each element using a 'for-loop'. Two 'for-loops' follow this; the first is used to calculate the moles of creosote using equation 3 and sums the initial total amount of moles of creosote for each compound for that time step. If the mole fraction in the creosote phase is greater than the solubility limit of that PAH in the creosote phase then a precipitation rate is calculated and the moles in the solid phase are calculated using equation 4. The mole fraction in the creosote phase is then set to the solubility limit and the aqueous phase solubility is set using equation 2. The moles of solid PAH are tabulated. The condition when the mole fraction of the PAH in the NAPL phase is less than the solubility limit (and solid PAH is present) is checked for. If this condition occurs, a redissolution rate is calculated and moles of PAH in the solid phase is calculated using equation 4. Again, the new solubility limit is set using equation 2 and the moles of solid PAH is tabulated. Finally, the concentration of PAH in the aqueous phase is calculated numerically using equation 1. The basic algorithm structure (just described) is provided in the appendix.

# V. Results and Accomplishments

**i) Characterization of sediment and capping materials.** The total concentration for 16 EPA priority pollutant PAHs in the Eagle Harbor Sediment was 1162 ± 108 µg/g. The individual PAH concentrations for bulk sediment and cap material are shown in Figure 3. The 2-3 ring PAHs dominated the distribution in Eagle Harbor sediment. The total PAH concentration in cap material was lower by four orders of magnitude (0.098 ± 0.012 µg/g). The PAH distribution in the cap material was different with more higher molecular weight PAHs present compared to the Eagle Harbor sediments. The Eagle Harbor sediment TOC was found to be 0.31 ± 0.01 % by weight. The low TOC and high PAH content of sediment raises an interesting observation that a majority of the TOC may be contributed by PAHs. The 16 priority pollutant PAHs comprise nearly a third of the sediment TOC. For tar-impacted manufactured gas plant sites, Hawthorne et al (2006) showed that the priority pollutant PAHs comprise about 40% of the total PAHs including the major alkylated homologs (a total of 34 PAHs). Thus, it appears that nearly all of the TOC may be explained by the contribution from parent and alkylated PAH compounds that may be present in the Eagle Harbor sediment. This observation may indicate the lack of an organic matter sorption phase in the sediment. In the absence of a sorbent organic matter phase, the PAH mixture may be present as a separate oil phase that coats the sediment inorganic particles, much like what may be expected from a creosote-contaminated sediment. Additional evidence of a creosote coating on particles is seen in the data for PAH distribution by particle size class. The distribution of PAHs in different size fractions of the Eagle harbor sediment and cap are shown in Table 1. As shown in Table 1, the PAH concentration is higher in the smaller particle sizes indicating a surface coating or surface adsorption phenomenon. The highest PAH concentration of 34,690 mg/kg is observed in the smallest particle size range (< 63 microns).

**Table 1. PAH distribution in four size fractions of Eagle harbor sediment.**

| Grain size<br>µm | Weight fraction<br>% | Total PAH<br>µg/g | PAH fraction<br>% by total |
|---|---|---|---|
| > 1700 | 5 | 969 | 2 |
| **170 – 1700 *** | **77** | **846** | **32** |
| 63 - 170 | 15 | 2,039 | 15 |
| < 63 | 3 | 34,690 | 51 |

* Used for column experiment; TOC content: 0.4 -+ 0.01 % by wt

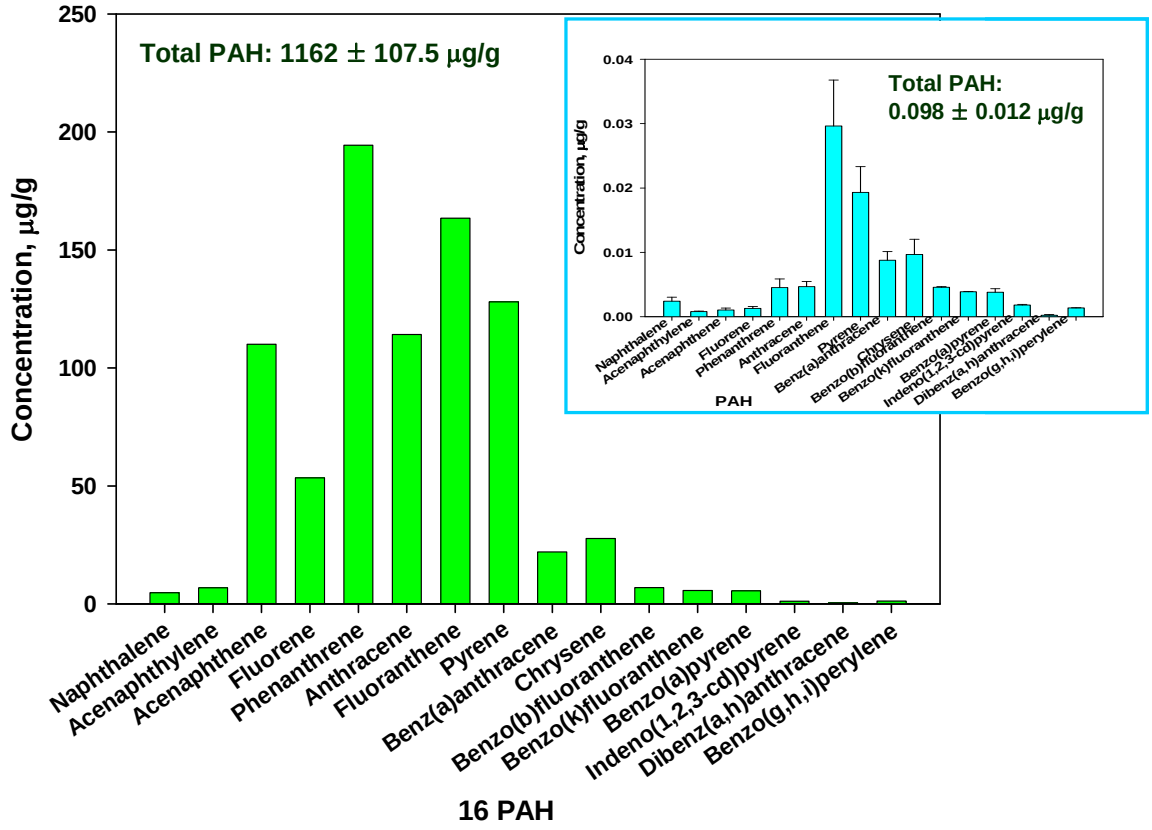


**Figure 3. The individual PAH concentration for bulk sediment and cap material (inset)**

A total of 16 EPA priority pollutant PAHs were measured to be 846 µg/g in the sieved Eagle Harbor sediment. PAHs such as acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene appear dominant. The higher molecular weight PAHs (greater than chrysene) are found in continually decreasing concentrations which is characteristic of pyrogenic PAHs associated with distilled, coal-derived liquids such as creosote (Brenner, R.C. et al. 2002; Stout, S.A., et al., 2001). The TOC of the sediment was 0.40±0.01% by wt. The percent organic carbon in the sediment after PAH extraction was found to be 0.09%, indicating that the extractable material (mostly PAHs) accounted for 77.5% of the TOC in this sediment. This would indicate a creosote content of 0.3%. The creosote content of the sediment was measured to be 0.002 g/g (0.2%) using the hexane/acetone extractables method. Some lighter molecular weight PAHs may have been lost during evaporation of hexane/acetone in the extraction method. The capping material had low initial PAHs (0.098±0.01 µg/g) and TOC (0.04±0.01% by wt.). Both the sediment and capping material used in this study have extremely low levels of native organic carbon.

**ii) Sediment-water equilibrium measurement.** Batch equilibrium tests were conducted using whole and sieved sediment. Sieving was performed using U.S. standard sieve numbers 80 and 12 to collect material between 180 and 1700 μm. As shown in Figure 4, the whole and sieved sediments gave nearly identical aqueous PAH concentrations, which is expected based on the mechanism of a creosote phase coating the mineral surfaces. The most abundant PAH in the aqueous phase was acenapthene followed by phenanthrene and fluorene. The concentration of PAHs larger than chrysene was barely detectable in the aqueous phase. As shown in Figure 5, the TOC normalized solid-water distribution ratios (log $K_{TOC}$) ranged from 4.3 to 7.1 and generally agreed well with literature values for PAH impacted sediments taken from Cornelissen et al (2006), Cornelissen and Gustafsson (2004), and Jonkers and Koelmans (2005).

The measured log $K_d$ values for sieved Eagle Harbor sediment, capping material, and peat moss amendment are shown in Table 2. The log $K_d$ values of the sediment are low (ranging from 2.2- 4.4) primarily due to the low organic carbon content in sediment. For peat moss, the measured $K_{oc}$ values are close to the predicted $K_{oc}$ values based on the frequently used correlation by Karichoff et al. (1979). In the capping material, organic carbon partitioning is low and plays a competing role for the sorption of PAHs with mineral surfaces. The expected $K_d$ due to organic carbon in the capping material was first estimated using published organic carbon-water partitioning coefficients ($K_{oc}$) (Hawthorne et al. 2006) and the capping material organic carbon content of 0.04%. For example, the $K_d$ for pyrene should be 16.3 L/Kg ($K_{oc} \times f_{oc} = 104.61 \times 0.0004$). In material that has a fraction of organic carbon ($f_{oc}$) less than about 0.001, sorption to mineral surfaces may play a significant role. This could lead to larger $K_d$ values in batch experiments than would be expected by organic carbon fractions alone (Mader, B.T. et al. 1997). However, the $K_d$ for pyrene in the capping material was measured to be only 6.10±4.36 L/Kg. It is expected that less pyrene would be sorbing to the cap in these experiments because they were done with a mixture of 13 PAHs ranging from naphthalene to chrysene. Competition for sorption sites may occur in these batch experiments resulting in lower $K_d$ values. When the capping material was heated at 400 °C for four hours, the $K_d$ was 3.77±1.50 L/Kg, indicating that labile (or amorphous) organic carbon contributed to some, but not all, of the sorption to the cap in these experiments. It has been theoretically demonstrated that at phenanthrene concentrations of 0.2 ug/L or greater, sorption to carbonaceous geosorbents (such as kerogen) begins to be less important than amorphous organic carbon (ratio of CG to AOC; 1:10) (Cornelissen, G. et al., 2005). Longer sorption times in the batch experiments can result in higher sorption of PAHs due to the small and perhaps inaccessible organic carbon fraction trapped in micropores or macropores of the capping material. Others have found sorption and desorption times of months to years are possible for PAHs entrapped in the organic carbon of soil and sediment pores (Pignatello, J.J, 1990 and 1995; Schuth, Ch. and Grothwahl, P. et al. 1994; Ran Y. et al. 2005).

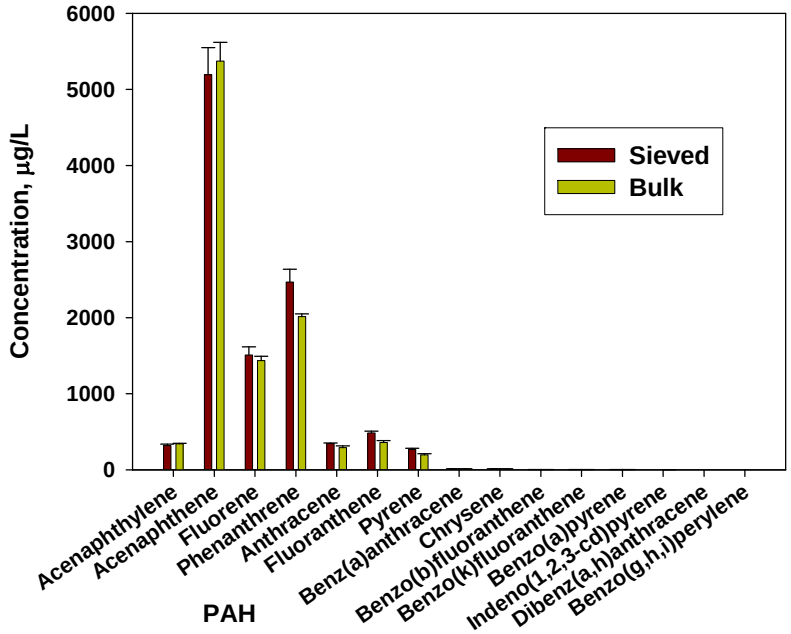


**Figure 4. Equilibrium aqueous PAH concentration for bulk and sieved fraction of PAH contaminated Eagle Harbor sediment.**

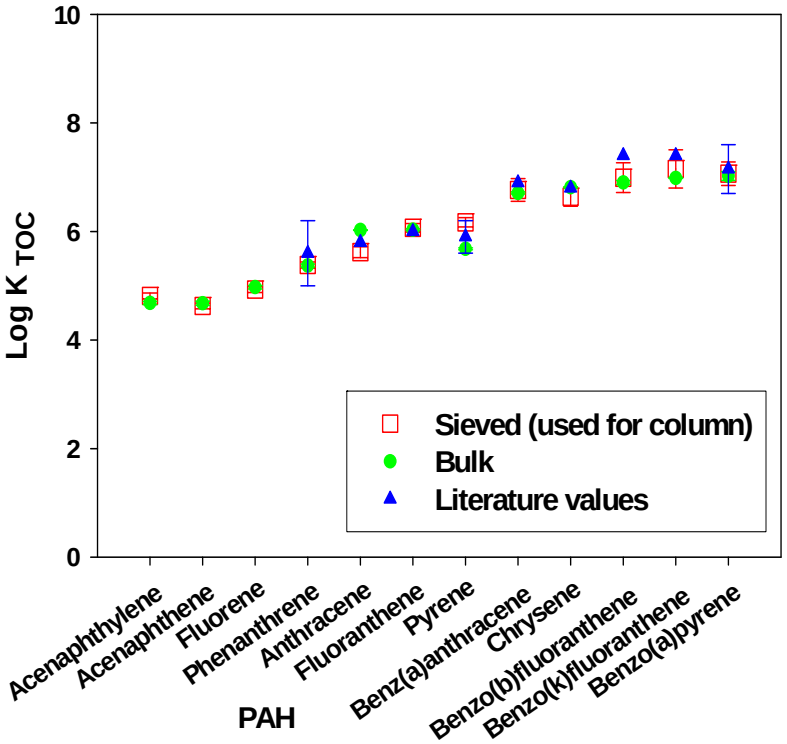


**Figure 5. TOC normalized solid-water distribution ratios (log $K_{TOC}$) of PAH**

**Table 2. Log $K_d$ values for Sieved Eagle Harbor Sediment, capping material, and peat moss amendment.**

| PAH | Log $K_d$ sediment | Log $K_d$ cap | Log $K_{oc}$ Peat Moss | Log Koc ($logK_{oc}$= 0.63 $logK_{ow}$) |
|---|---|---|---|---|
| Naphthalene | 2.24±0.13 | 0.35±0.21 | 3.28±0.23 | 3.09 |
| Acenaphthalene | 2.21±0.07 | 0.28±0.19 | 2.66±0.42 | 3.73 |
| Acenaphthene | 2.03±0.07 | 0.23±0.18 | 2.79±0.32 | 3.71 |
| Fluorene | 2.30±0.05 | 0.30±0.15 | 3.45±0.11 | 3.97 |
| Phenanthrene | 2.82±0.03 | 0.64±0.07 | 3.95±0.08 | 4.25 |
| Anthracene | 3.40±0.05 | 1.48 ±0.39 | 4.37±0.18 | 4.24 |
| Fluoranthene | 3.49±0.03 | 1.41 ±0.13 | 4.56±0.30 | 4.74 |
| Pyrene | 3.63±0.03 | 1.38 ±0.09 | 3.84±0.11 | 4.67 |
| Benz(a)anthracene | 4.01±0.06 | 1.98 ±0.18 | 5.75±0.15 | 5.45 |
| Chrysene | 4.29±0.05 | 2.04 ±0.06 | 5.61±0.11 | 5.45 |

**iii) Column studies without amendments.** Column studies were conducted first without amendments to evaluate breakthrough of PAHs under advective conditions. Breakthrough is defined as the bed volumes (or time) at which effluent (port 6) concentrations are 50% of sediment pore water (port 1) concentrations (BT50). Figures 6 and 7 show data from a column with no amendments initially, and after 8 bed volumes have passed. Hollow symbols represent data below the limit of quantification (LOQ) or above the calibration range. Initially the PAHs were not distributed throughout the entire cap layer and then after 8 bed volumes the PAH concentrations went beyond the BT50 (breakthrough probably occurred between 5-8 bed volumes). Benz(a)anthracene and chrysene pore water concentrations still decreased along the length of the column after 8 bed volumes. This is due to their low water solubilities and higher sorption to solids relative to the other PAHs measured. Initially naphthalene appears at higher concentrations in the cap near the sediment (port 2) than in the sediment layer (port 1). This is possibly due to the migration of

naphthalene in porewater during column construction. During column construction, PAHs such as naphthalene reside in sediment porewater and small amounts of water overlying the sediment. Sediment porewater and sediment overlying water becomes incorporated in the pore water in the capping material closest to the sediment, carrying PAHs to lower levels in the cap (ports 2 and 3). As seen in Figures 6a, there appears to be little retardation of PAHs in the column. Even the expressed water during cap placement transports low molecular weight PAHs nearly half way through the cap in the column. After 8 bed volumes all the PAHs have broken through the sand cap (Figure 6b). Naphthalene is seen to be depleting in the sediment layer (port 1) likely due to the higher aqueous solubility and mobility of this compound. Other low molecular weight PAHs appear to deplete during the length of the experiment because they are readily released from the creosote phase, while high molecular weight PAHs such as pyrene, benz(a)anthracene, and chrysene continue to increase in the sediment pore water throughout the length of the experiment.

Based on these experiments, it appears that measuring pore water concentrations is critical in determining breakthrough of PAHs in a cap. When solid phase PAH concentrations are used, the degree of pore water transport could be underestimated in cases where the cap has low sorption capacity. Based on the low $K_d$ values of the capping material (Table 2), very little of the PAHs are expected to adhere to the cap. The expected PAH concentration in the capping material was calculated based on the measured $K_d$ values for the cap and porewater concentrations. Also, at the end of the column experiment, the column contents were frozen in dry ice and sectioned for PAH extraction and measurement. The results of PAH measurement in cores taken out of the cap in the field is compared with measurements from the laboratory column and modeling predictions in Figure 7. The results are presented as total PAH concentration profile as a function of distance from the sediment-cap interface. The PAH concentrations in the field cap range from 0-20,000 μg/kg , with the higher concentrations near the sediment-cap interface. These concentrations seen in the cap can be considered close to the background levels of PAHs often found at harbor sites (Magar, V.S. et al., 2007). The measurement of 16 PAHs obtained from the laboratory experimental column compared well with PAH measurements from field cap cores (Figure 7). The modeling predictions based on the partitioning between porewater and cap material also is in the range of measured values in the field and laboratory. A key conclusion of this comparison is that measurement of PAH concentration in cores taken out of sediment caps is a poor indicator of contaminant breakthrough, especially in cases where there is little capacity in the cap material to sorb contaminants. In-situ porewater concentrations need to be measured to provide an assessment of contaminant movement through caps.

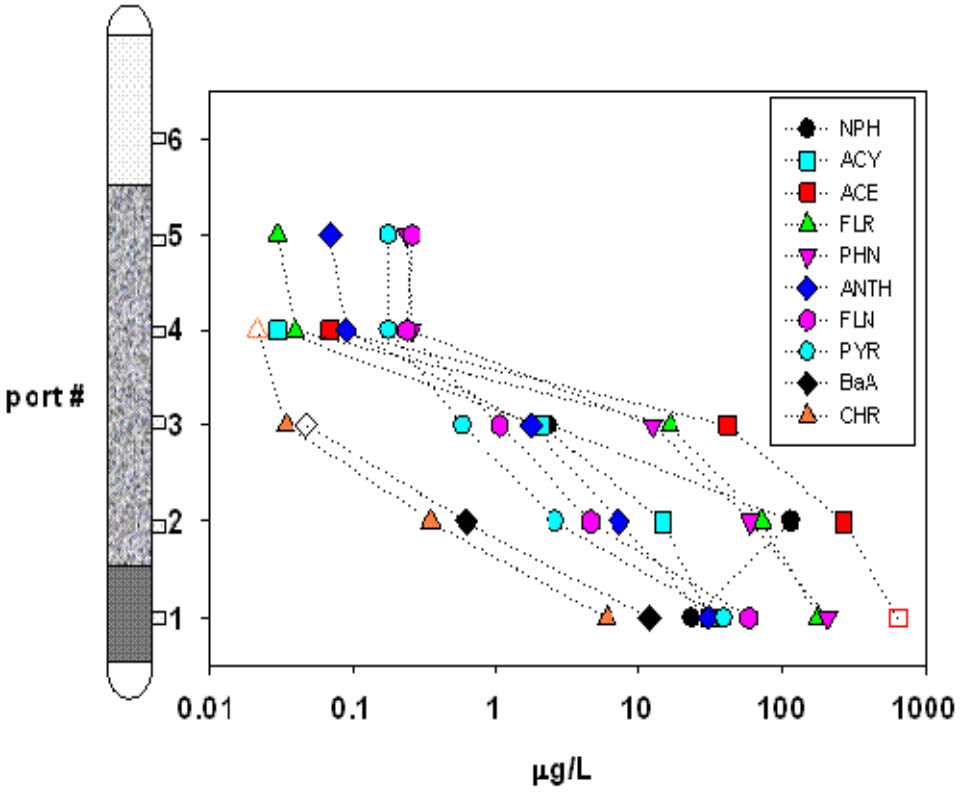


**Figure 6a. Initial PAH distribution in sediment and cap without amendments**

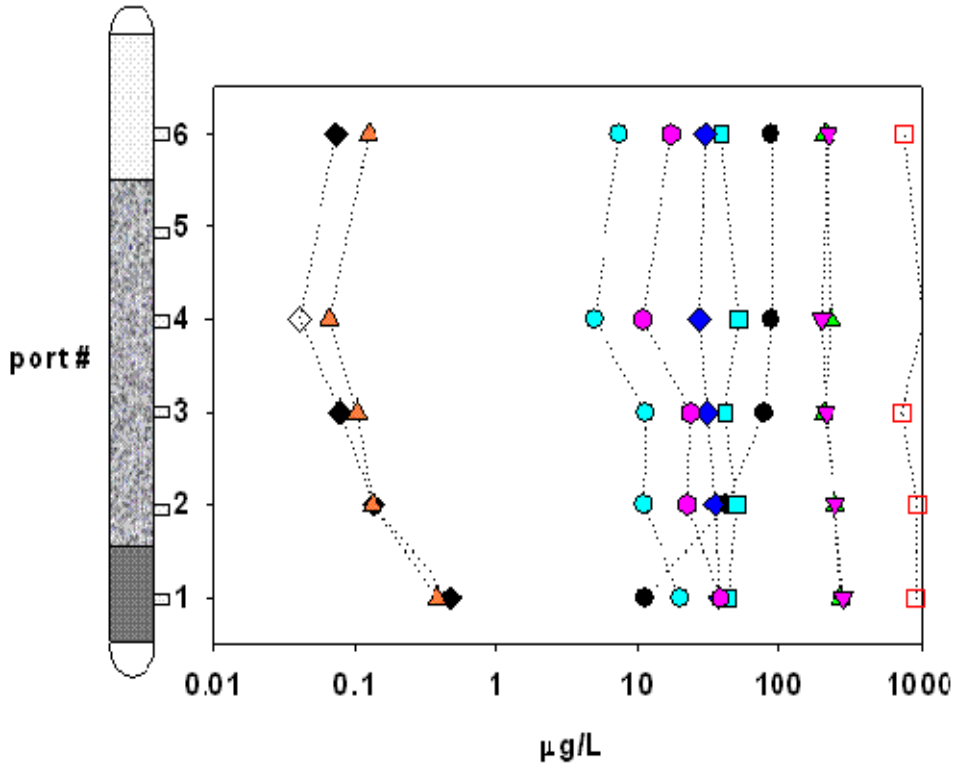


**Figure 6b. PAH Breakthrough after 8 bed volumes in a cap with no amendments.**

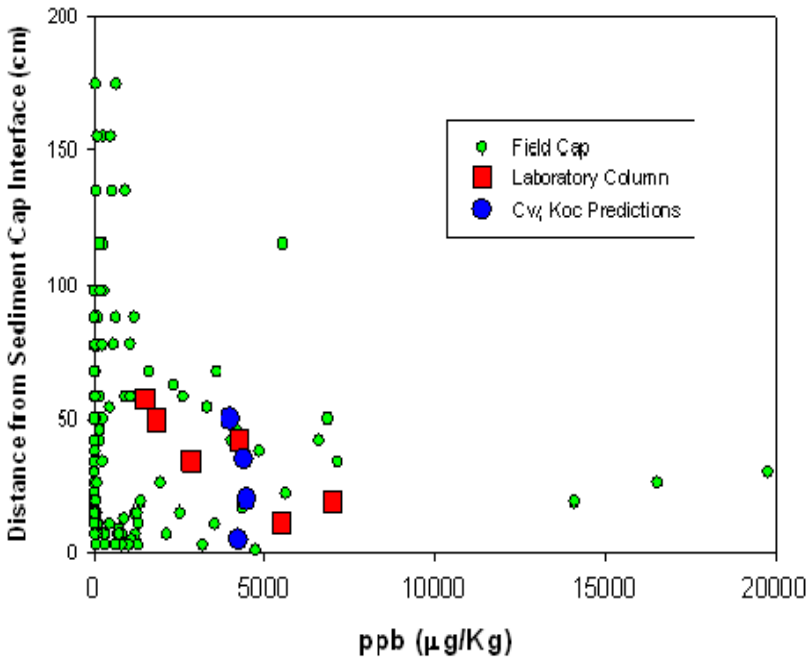


**Figure 7. PAH measurements in a field cap (Sass et al., 2009) compared to measurements in a laboratory column and theoretical predictions.**

**iv) Column studies with amended caps**

Peat moss amendment. Column studies with amendments were conducted to explore the potential retardation of PAH migration in the cap. Columns with 2% TOC amendment in the form of peat moss created a lot of backpressure and flow rates of 25 ml/hr could not be achieved. In a column with 0.2% TOC amendment, adequate flow rates could be maintained and a delayed breakthrough of PAHs occurred (Figure 8). Slight turbidity was observed (3.3 NTUs) initially in the column effluent, but reduced to 1.4 NTUs within a week. This level of turbidity is not expected to correspond to dissolved organic matter levels that would affect the SPME measurement. SPME fibers have been used to measure PAHs in dark brown coal wastewater with DOM concentrations as high has 350 mg/L (Poerschmann, J., et al., 1998). The migration of PAHs in a column amended with 0.2% TOC was slower than that observed in columns with no amendment. Breakthrough of naphthalene was observed after 6.2 bed volumes and other light PAHs after 46.5 bed volumes. Pyrene concentrations in porewater from port 4-6 remained an order of magnitude less than pore water concentrations from the sediment layer (port 1). Porewater concentrations of pyrene from the sediment layer continued to increase even after 150 bed volumes.

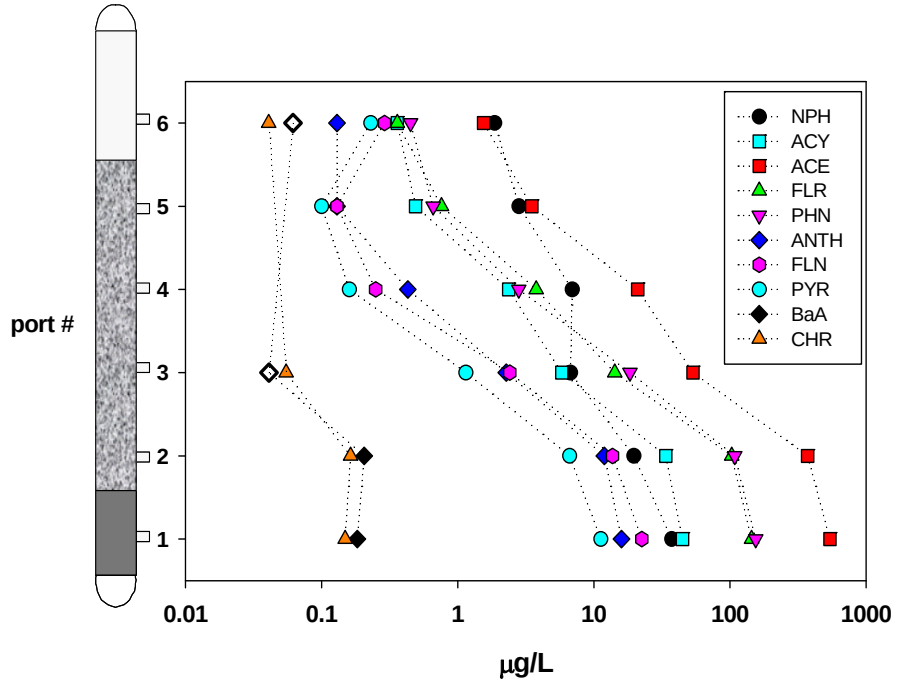


**Figure 8a. Early PAH profile in a cap with peat moss amendment (1.9 bed volumes).**

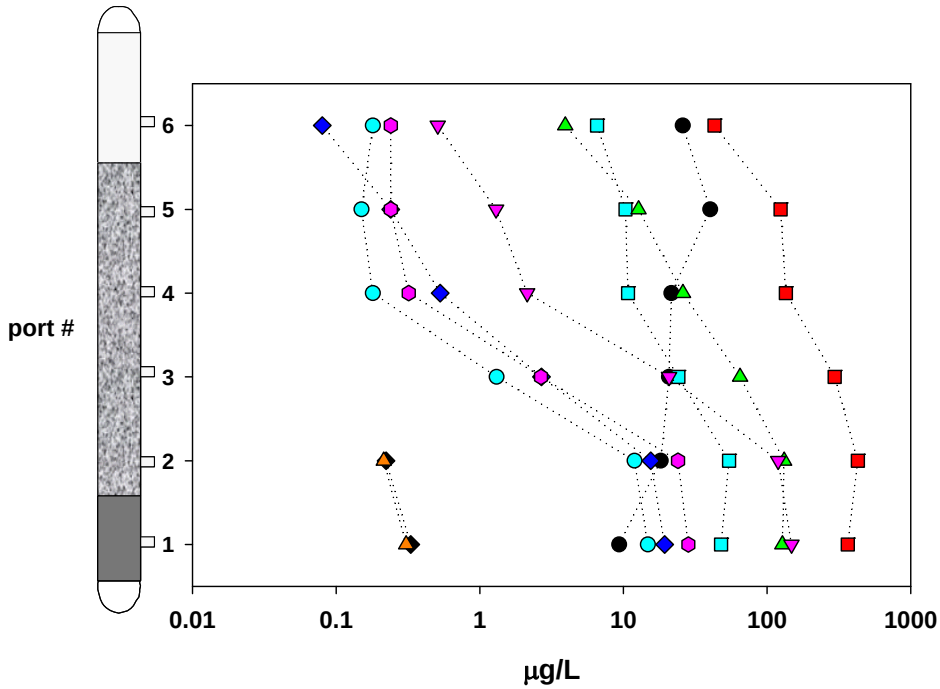


**Figure 8b. PAH Breakthrough after 11.3 bed volumes in a cap with peat moss amendment.**

Activated carbon amendment. Activated carbon (AC) at 0.2 and 2% dry weight was added to the capping material in separate columns. It can be seen that 2% GAC greatly reduced the transport of PAHs after 18 bed volumes (Figure 9). In 0.2%GACamended columns, concentrations remain low in the capping material, however, they did reach detectable levels of the PAHs. The low molecular weight PAHs depleted faster from the sediment porewater for the 0.2%GACcolumn than in previous experiments, making the 2% GAC column a better comparison to the column with no amendment. With 2% AC, the capping material (ports 3-5) remained well below quantitation levels for the length of the experiment. High molecular weight PAHs were slightly above quantifiable levels in the capping material at port 2. This transport is most likely due to porewater PAH displacement during column construction (not due to sediment consolidation). PAH detection may also be attributed to the slower rate at which high molecular weight PAHs (e.g. pyrene) enter pores in the GAC relative to low molecular weight PAHs (e.g. naphthalene). Accessibility of pollutants to black carbon pore networks is dependent on pollutant molecular size (Zhu, D. et al., 2005).

Visually the water samples appeared to be clear for every column except for the initial samples from the column amended with peat moss. Solid phase microextraction using an internal calibration with deuterated (d-PAH) internal standards for each PAH measures total dissolved PAHs (freely dissolved and DOM associated) (Poerschmann, J. et al. 1997; Poerschmann, J. et al. 1998). However, at low turbidity (<1.4 NTU) for the PAHs measured, the DOM fraction is small relative to the freely dissolved concentration. Figure 9A-9H. show all the data for a middle and high molecular weight PAH (phenanthrene and chrysene) over many bed volumes at the sediment layer (port 1) and the overlying water (port 6) for each column. From these graphs it is apparent that GAC is an effective amendment, but that peat moss (0.2% TOC) was also somewhat effective for the high molecular weight PAHs (e.g. chrysene).

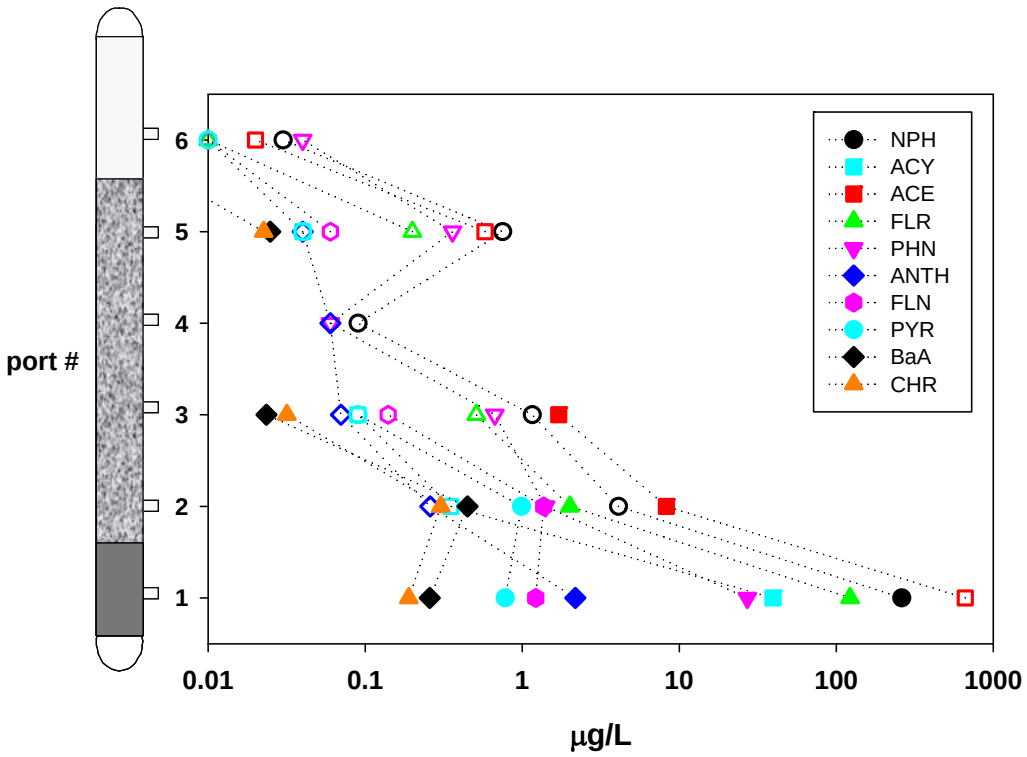


**Figure 9a. Initial PAH profile in experimental cap amended with 2% activated carbon.**

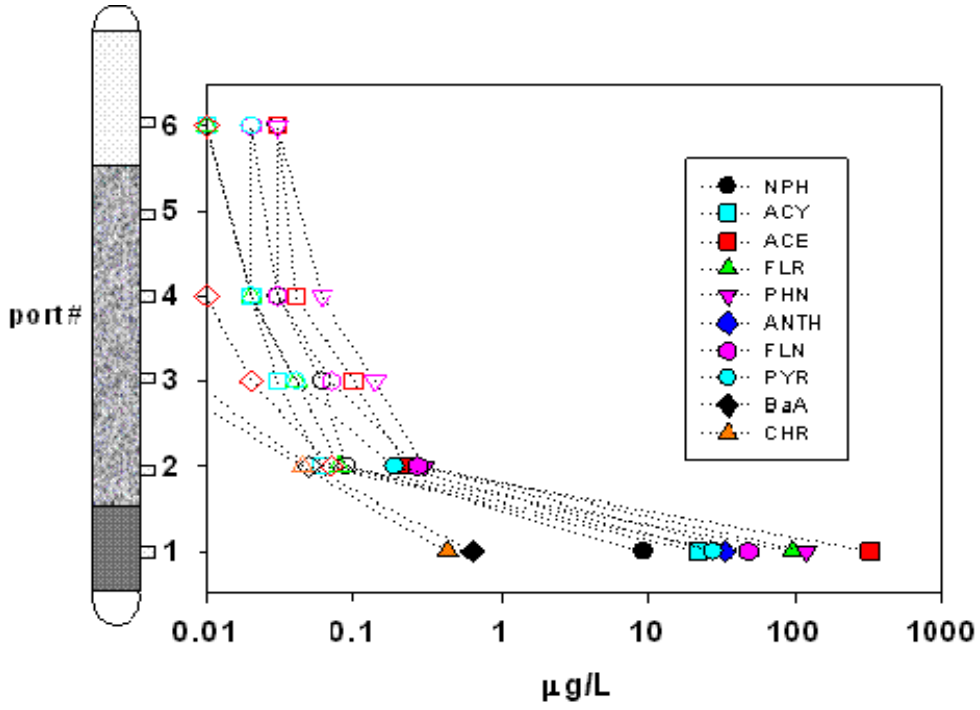


**Figure 9b. PAH profile in experimental cap amended with 2% activated carbon after 18 bed volumes.**

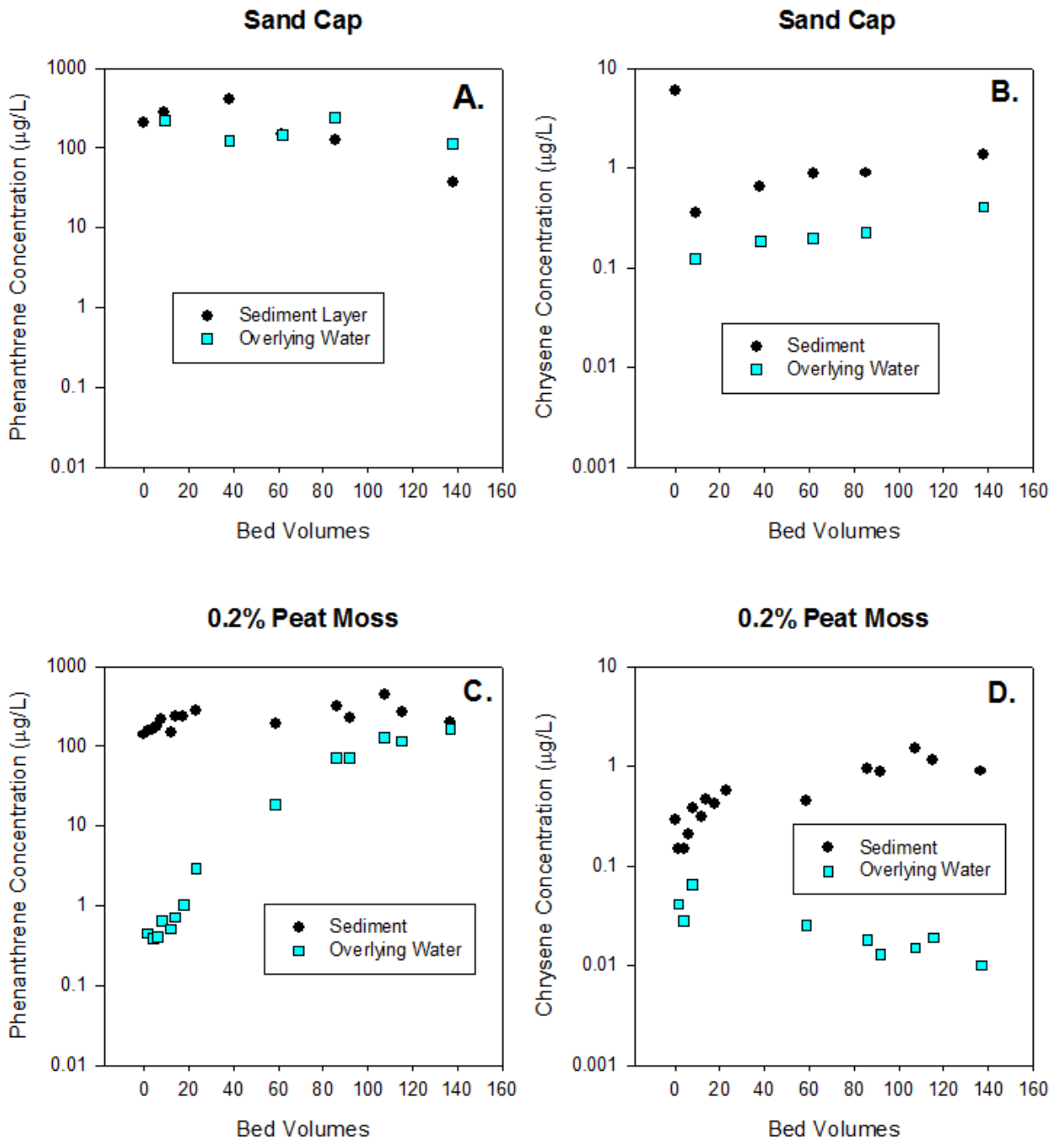


**Figure 10. Phenanthrene and chrysene concentrations as a function of bed volumes in sediment caps without amendments and with peat moss amendment.**

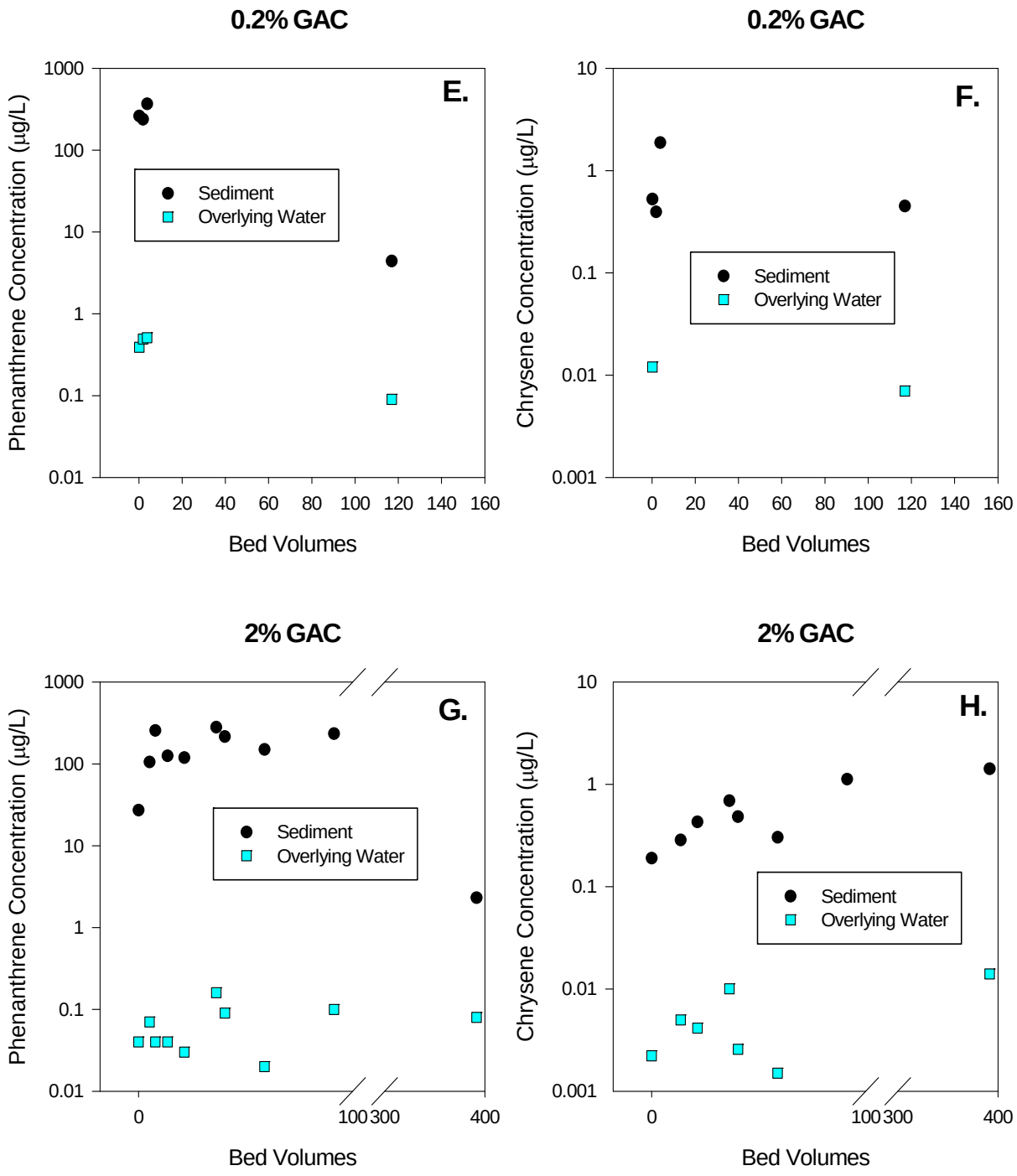


**Figure 11. Phenanthrene and chrysene concentrations as a function of bed volumes in sediment caps with 0.2% and 2.0% activated carbon amendment.**

**v) Aqueous equilibrium experiments with sediment before and after flushing with water.**

Sediment from the column studies were analyzed for PAH dissolution before and after exposure to flow in column experiments. These measurements were performed to evaluate how PAH dissolution changed as a function of exposure to water flushing in the column experiments. We expected to see a loss of the lower molecular weight PAHs from the sediment as a function of flushing. Sediment from two column experiments were taken after 4 months and 7 months of flow as described in results presented earlier for the unamended column experiments. The sediments were placed in batch vials with a solid to liquid ratio of 0.04 and allowed to equilibrate in the dark for 6 weeks. The water phase contained 1000mg/L $NaN_3$ as a biocide to minimize biological activity during the equilibrium experiment. Batch equilibrium experiments were also performed using sediment that had not been in a column, but was representative of the sediment initially placed in the columns. Low molecular weight PAHs were greatly reduced in both columns based on porewater measurements and batch experiments. Figure 12 shows the drastic reduction of acenaphthene (ACE) in batch experiments of the sediment placed in columns relative to sediment that had not been in a column. Other low molecular weight PAHs such as naphthalene and acenaphthylene appear to have depleted in the initial sediment.

In a column run for 4 months the acenaphthene concentration in the porewater collected at the end of the column experiment was 1.05 ug/L (not shown in a figure). When this sediment was placed in the batch experiment the acenaphthene concentration in the water phase doubled to 2.16 ug/L. This is possibly due to the greater contact between the sediment and the water phase in a batch experiment. In the column, many of the solid surfaces are touching other solid surfaces and not in contact with the water phase. In addition to this, there may be pore spaces which are not hydraulically connected to the flow of water though the column or the porewater sampling port. When the sediment is removed from the column and introduced in a batch slurry there is better contact between the water phase and contaminated sediment surfaces.

For a middle molecular weight PAH such as phenanthrene (PHN), a smaller decrease in equilibrium aqueous concentration is seen compared to acenaphthene. After 4 months in a column, aqueous equilibrium phenanthrene concentration is reduced by about half and is decreased further after 7 months in a column. Phenanthrene porewater concentration in the sediment collected from the column at the end of the 4 month experiment was at 37 ug/L (not shown in the figure) and only 18.4 ug/L from the batch experiment using the same sediment. It is possible that the creosote phase exposed to fluid flow in the columns may have developed an increased mole fraction of phananthrene after 4 months. When this sediment is placed in a batch experiment, the fresh creosote surfaces that are now exposed do not

contribute additional phenanthrene to the porewater relative to the creosote surfaces that had already been exposed in the column and been enriched in phenanthrene.

For pyrene, there appears to be little change in aqueous concentration as a function of exposure to water flushing in the columns. This could be a result of the loss of pyrene mass being compensated by the faster loss of low molecular weight PAHs resulting in little change in the mole fraction of pyrene in the residual creosote phase. For a high molecular weight PAH , chrysene, (CHR) the concentrations in the batch water phase from the column material is higher than the sediment that was not placed in the column. This likely a result of the increased mole fraction of chysene in the creosote phase of the sediment that was in the columns. Like phenanthrene, chrysene measurements from batch experiments after the column was run were smaller than porewater measurements at the end of the column. This can be explained for reasons similar to phenanthrene where the creosote trapped in immobile zones did not undergo change in mole fraction while the surfaces exposed to flow in the column were enriched with the higher molecular weight compounds.

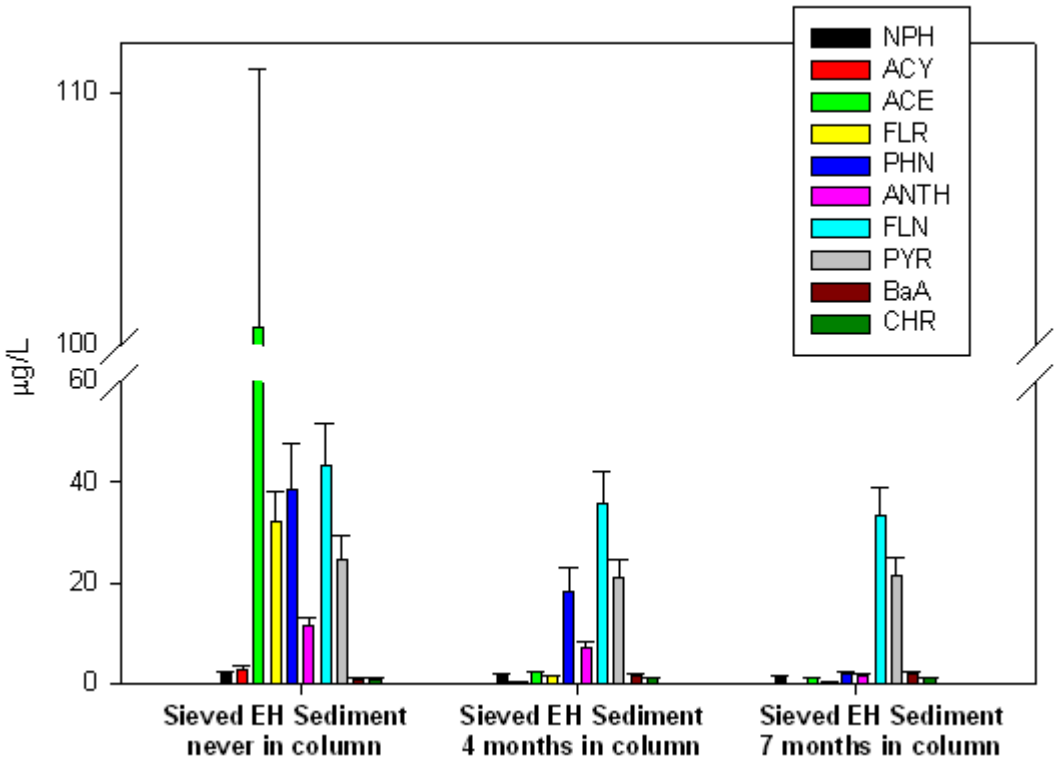


**Figure 12. Eagle Harbor (EH) Sediment that was analyzed in batch equilibrium experiments (solid:liquid ratio 0.04) after it had been subjected to various stages of dissolution.**

**vi) PAH Migration in Biological Column Experiments**

Azoic column experiments were performed to understand the effects of groundwater advection on PAH transport in Eagle Harbor capping material. A second scenario was desired to understand the effects of groundwater advection on PAH transport in biologically active systems. This is important because PAHs (once in the aqueous phase) can be significantly degraded (Wammer et. al. 2005, Bosma, T.N.P., et al. 1997). PAHs on the sediment-water surface have been suspected to degrade (Xia, X. et al. 2008). Bacteria attached to porous media can also increase the sorption capacity of the cap and degradation of those sorbed PAHs may also be possible (Hernan, D. C. et. al. 1997). Here, we sought to establish an optimal degradation experiment under aerobic conditions. In areas of groundwater upwelling, oxygen from the surface may be limited. However, anaerobic degradation may be possible with nitrate or sulfate serving as electron acceptors. Anearobic degraders have been shown to degrade PAHs utilizing nitrate (McNally, D.L. et al. 1998), but the degradation rates are typically much slower compared to aerobic degradation.

First, a column was set-up and run without the addition of sodium azide. This column performed similar to systems with sodium azide (breakthrough of PAHs in the cap was rapid), and it was concluded that the column may not have been biologically active simply because the column was not killed with sodium azide. At this point, the sediment and capping material from Eagle Harbor had been stored at 4 degrees C for over a year. Both aerobic and anaerobic PAH degrading bacteria have been isolated from the Eagle Harbor site (Geiselbrecht, A.D. et al. 1998, Hedlund, B.P. et al. 2006, Tang, Y.J. et al. 2005). However, the native bacteria may have been inactive, or there may have been insufficient nutrients supplied by the sediment. In order to test for the presence of PAH degrading bacteria in Eagle Harbor sediment, batch experiments were conducted. Batch experiments were also conducted using freshly collected Anacostia River sediment. In addition, recent literature on sediment from the Anacostia River suggested that PAH degraders would be present and should be able to colonize a cap (Himmelheber, D.W. et al. 2008, Himmelheber, D.W. et. al. 2009).

The batch slurry experiments were started in 50 ml glass flasks containing 5 grams of sediment and about 40 ml of nutrient solution. The nutrient solution was selected based on work by previous researchers who used BOD nutrient buffer pillows (Knightes et al. 2003), and nutrient mixtures from other researchers were considered (Wammer et al., 2005, Ripp et al. 2000). The flasks were capped with a foam plug to allow for aerobic conditions, but prevent the volatilization loss of low molecular weight PAHs. The flasks were placed on a shaker table and allowed to incubate while the contents were mixed up in a slurry. After two weeks, the sediment suspensions were considered ready to be used to seed batch culture experiments. Culture experiments were first repeated in 50 ml flasks and then repeated using

larger containers. Final culture batches were conducted in 4L flasks containing Teflon stir bars with large foam plugs. The batch cultures received a nutrient solution, a phenanthrene spike (2.25 ug) initially in methanol (15µL), and 5 drops of bacterial seed from the sediment slurries (both Eagle Harbor and Anacostia River). The small quantity of methanol present in spikes of 15 µL was not expected to impact micro-organisms or have an impact on biomass microbial activity (Knights, C.D. 2003). However, if bacteria were growing on methanol as a food source, the higher biomass could increase sorption of PAHs. Bacteria from the sediment slurry may have also contained a small amount of sediment. This would have had a larger effect on the smaller 50ml batch experiments than the larger 500ml or 4L ones. Figure 13 shows the results of phenanthrene measurements in the aqueous phase of the 50 ml batch experiments using SPME with alum flocculation.

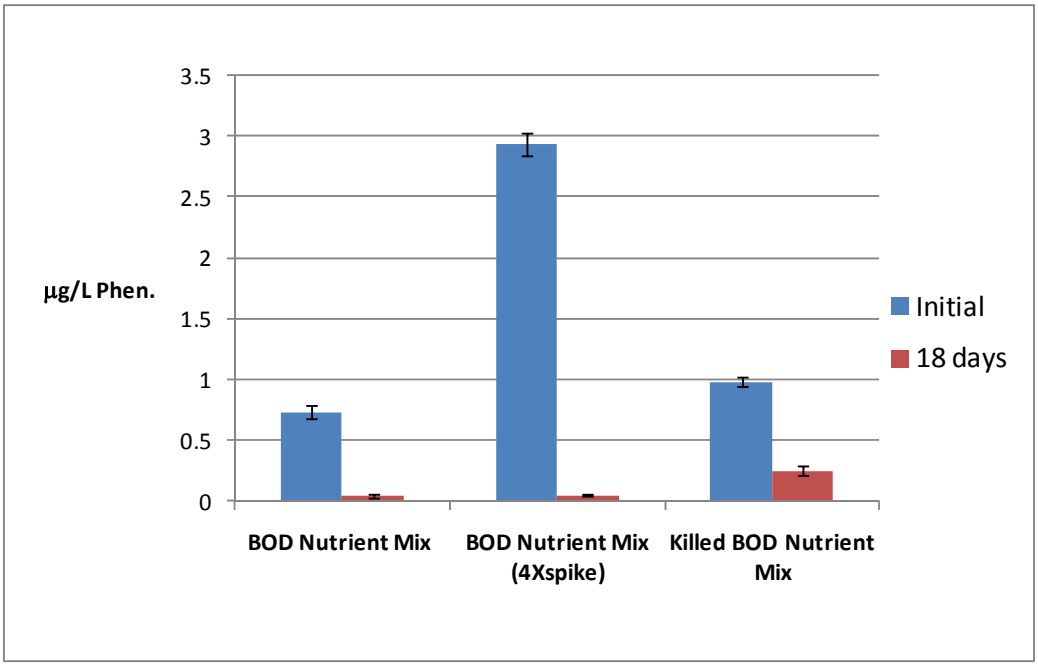


**Figure 13. Phenanthrene depletion in 50 ml Batch Culture Experiments.**

It can be seen that after 18 days, phenanthrene loss was observed in all batch experiments. It appears that the greatest removal occurred in experiments with no sodium azide added. Error bars represent one standard deviation and are based on 2 to 4 replicates. It was suspected that initial losses of phenanthrene in the BOD nutrient mix over the killed (500mg/L $NaN_3$) BOD nutrient mix was due to fast

degradation (in the BOD nutrient mix) or sorption of PAHs to biomass. The killed BOD nutrient mix may have showed a depletion of phenanthrene due to sorption to sediment in the bacteria seed or sorption onto dead biomass. In order to minimize sorption of PAHs onto organics introduced with the bacterial seed, larger batch culture experiments were performed. These second set of experiments were performed in larger 500ml jars with Teflon stir bars to maintain well mixed conditions. These larger experiments were again capped with a foam plug and were sampled initially, and at 4 and 10 days (Figure 14).

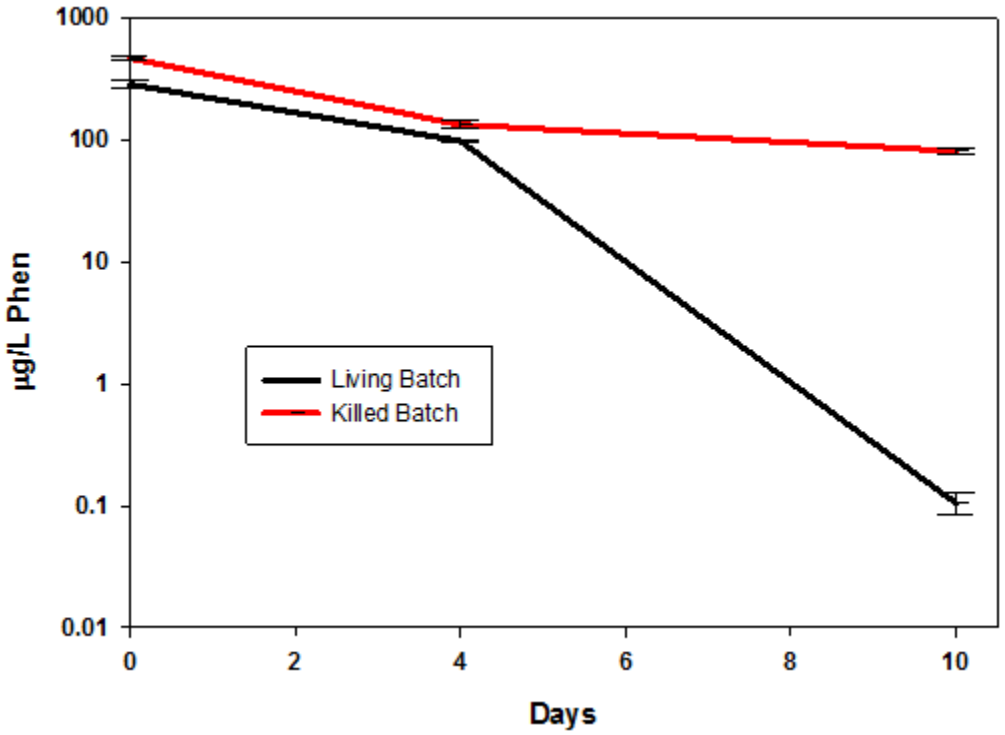


**Figure 14. Phenanthrene depletion over time in biologically active and inactive batch experiments.**

The experiment shown in Figure 14 shows that phenanthrene could be depleted to levels several orders of magnitude smaller than starting concentrations when the batch system was not killed with sodium azide. Both the "living" and killed experiment were spiked with the same amount of phenanthrene (8000 ug) dissolved in methanol (40uL) and spiked with 2ml of bacterial seed. The only difference was the presence of sodium azide or small variations in the suspended solid content or biomass content of the bacterial seed. Again, losses were seen in both batch experiments. In the batch killed with sodium azide, the rate of loss was much greater during the first four days compared to the latter period.

It was suspected that we might be observing the sorption of PAHs onto bacteria growing on methanol. To check for this possibility, phenathrene dissolved in methanol was spiked into an empty glass

jar and the methanol was allowed to evaporate overnight. The glass jars were then filled with water and the phenanthrene was allowed to dissolve into the water phase and a solution of 178 μg/L phenanthrene was produced within a few days. This solution was used in three batch experiments. First, a batch experiment with nutrients and a bacterial seed. Second, a batch with nutrients and no bacterial seed. Third, a killed batch with nutrients and a bacterial seed. In the first batch, the phenanthrene concentration depleted to 1.3 μg/L after 4 days. In the second batch, with no bacterial seed, the concentration decreased to 72 μg/L, and the killed batch concentration showed a measured increase to 262 μg/L after 4 days. Calibration checks showed that the SPME calibration was valid. It is uncertain what caused the concentration changes in this final experiment.

With the confirmation of PAH degrading bacteria in the culture solutions, the first biologically active column experiment was started. A 4 L batch culture was created and allowed to deplete the phenanthrene concentration down to 1.9 μg/L. At this point, the absorbance of the solution was measured at 660NM to be 0.016, which is the wavelength often used for estimating biomass concentration via optical density (Koch, A.L., 1994).

Column experiments were constructed using capping material that had been innoculated with the PAH degrading bacterial culture. The configuration of this biological column was slightly altered from that of the earlier azoic columns. A thin layer of glass beads was placed between the sediment and the capping layer in the biological column. An effort was made to place port 1 at this layer of glass beads to get a more accurate measure of the PAH inputs to the cap. However, due to some settlement of either the glass wool below the sediment, or the sediment itself, port 1 ended up being located 1 cm into the capping material. This can be seen in Figure 15 on the column depicted on the y-axis. It can also be seen that the distance of the overlying water (OW) was shortened (to 9.5 cm) and sampling of this layer was not done through a port, but rather, using a glass Pasteur pipet from the top of an open column. Column effluent was allowed to overflow out of port 6. The length of the capping material remained the same (65 cm) and the sediment layer was shortened (to 10 cm). The biological column was operated for 71 days with the last sampling taken at 48 days (91.7 bed volumes). Porewater concentrations have been measured for 12 PAH compounds from 5 ports along the cap and the overlying water. In addition to the small structural changes, it is likely that the source zone is different compared to earlier azoic columns. This makes it a little difficult to make direct comparisons between the azoic and this biologically active column. However, if we take port 1 concentrations to be a source input to the rest of the cap, it is possible model the system using CXTFIT code. Figure 15 focuses on the migration of phenanthrene through the biological cap for various bed volumes (listed in the legend). At low bed volumes (initially) phenanthrene concentrations are high at port 1 (inlet) and progressively decreases up through the column. However,

after only 2 bed volumes (green diamonds in Figure 15), phenanthrene appears halfway through the cap. At longer times, the source of phenanthrene in sediment appears to have depleted and the higher concentrations are seen near the top of the cap as the PAHs are flushed out of the cap. Thus, there appears to be little improvement of PAH breakthrough in a biologically active sand cap over an azoic sand cap. Overlying water concentrations are indicated by corresponding solid lines at the top of the figure.

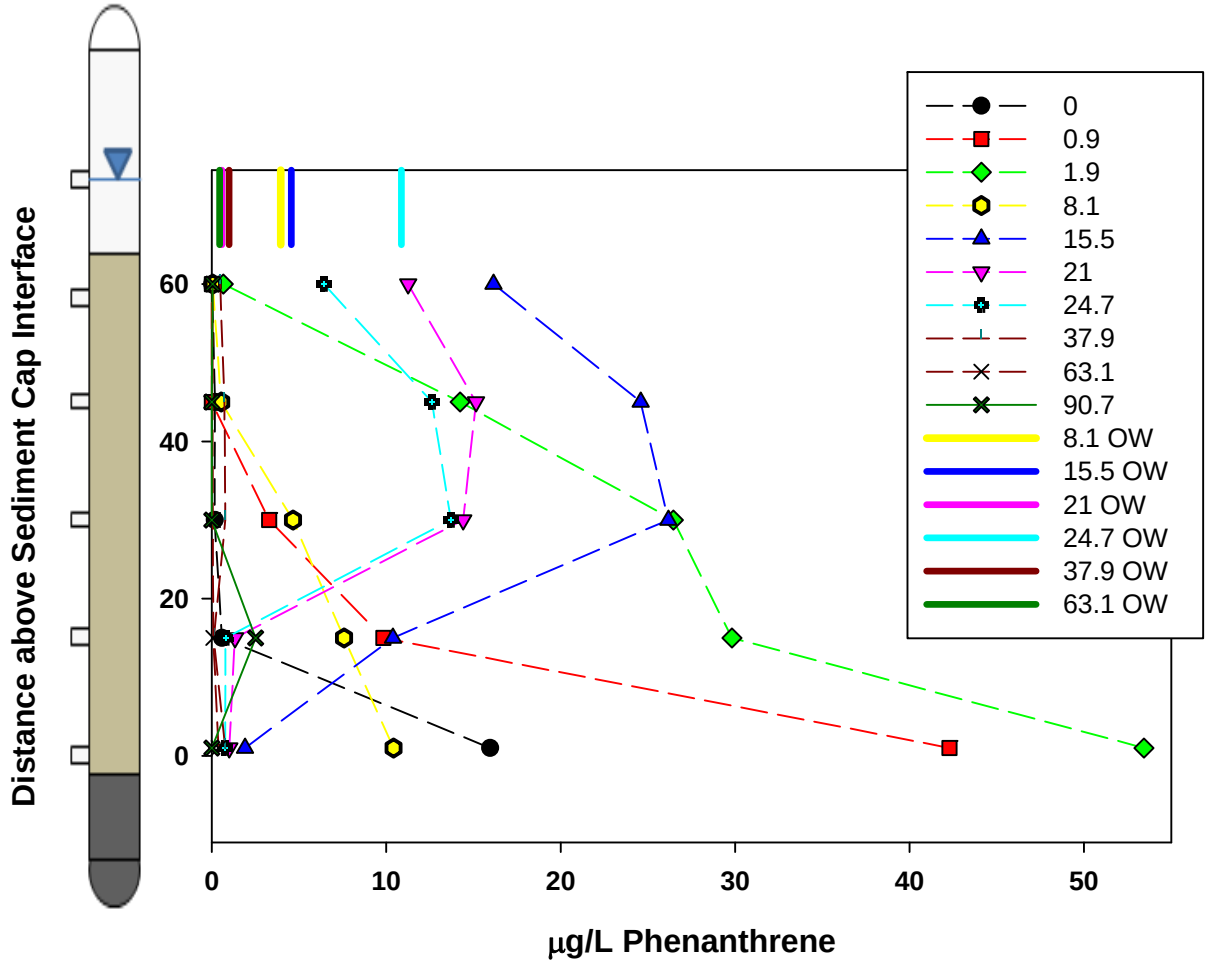


**Figure 15. Migration of Phenanthrene through the biologically active capping material at different bed volumes (indicated by the numbers in the legend)**

**vii) Modeling PAH migration in sediment caps**

The mathematical model for PAH dissolution from the creosote phase was used to predict the change in PAH concentrations in the creosote phase and water phase as illustrated in Figures 16 and 17. However, aqueous concentrations of low molecular weight PAHs in our model don't drop off as rapidly as in the model produced by Peters et al. (1999) which is likely due to differences in the implementation of the mass transfer rate constants. Additionally, when conducting model verification, the mass balance for two PAHs (anthracene and chrysene) do not close. These are the two PAHs that were expected to form a solid precipitate (Peters, C. et al., 1999).

As seen in Figure 16, the concentration of naphthalene is depleted rapidly in the first few years of flushing at typical groundwater velocities. However, the higher molecular weight compounds such as chrysene is seen to increase in concentration with time due to the much faster loss of the low molecular weight compounds. This phenomena is manifested in the aqueous concentration as well in Figure 17, where, the lower molecular weight compounds are seen to decrease with time and the higher molecular weight compounds are seen to increase with time.

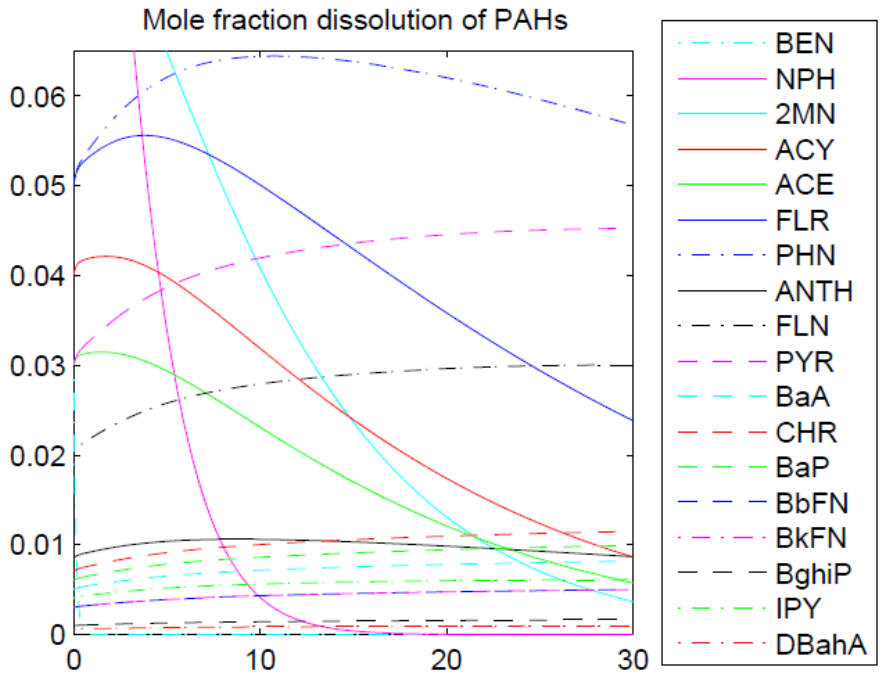


**Figure 16. Mole fractions of PAHs in the creosote phase over 30 years.**

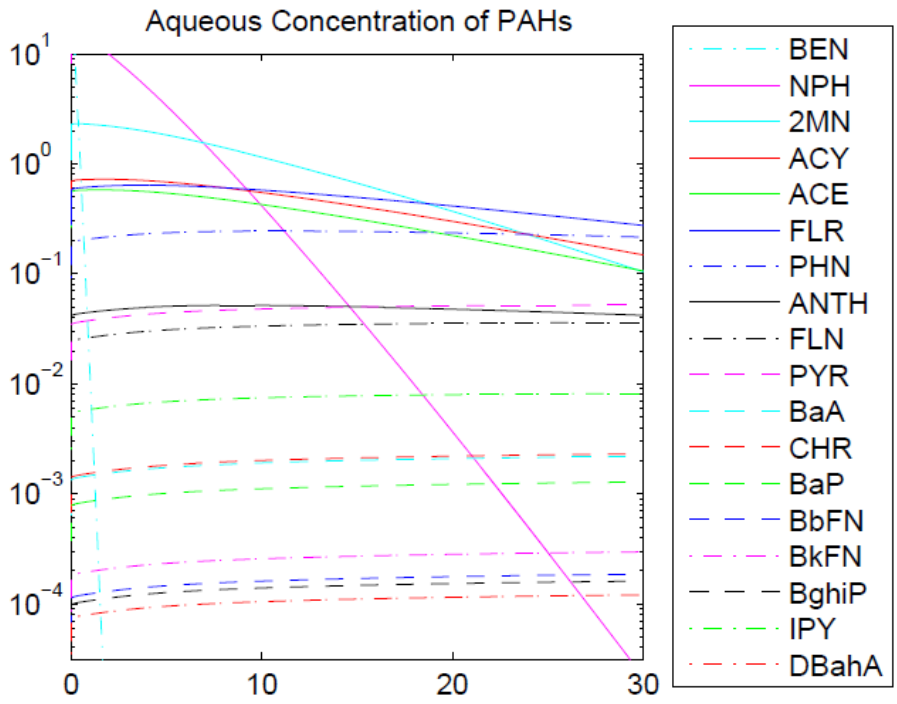


**Figure 17. Aqueous PAH concentrations in the pore water over 30 years**

The observed migration of PAHs though the capping material was modeled using an analytical solution to the one dimensional advection-dispersion equation with retardation (Ogata and Banks, 1961). Pyrene was chosen to be used in the analytical model because its concentration in the sediment layer remained relatively constant for the duration of the experiment, and a constant boundary condition was a reasonable assumption. A constant influent pyrene concentration in the porewater from the sediment layer ($C_0$) was assumed to be the average of the observed sediment porewater concentration for the analytical model. A tracer test shown in Figure 18 was used to obtain a pore velocity of 121 cm/day (126.5 cm/day for 0.2% TOC amended column) and an effective porosity of 0.25 (0.24 for TOC amended column). Chloride was assumed to be a conservative tracer for columns with and without amendments. Others have found that chloride can be retarded by cytoplasts (closed pores) in pure peat systems (Price et al., 2009). The assumption is being made that the small peat moss contents mixed in these columns does not impact chloride retension. A column length of 60 cm was used for the tracer studies (cap only) and was used for calculations. The linear hydrodynamic dispersion coefficient (D) was 225 $cm^2$/day (155 $cm^2$/day for TOC amended cap). The capping material bulk density ($\rho_b$) was taken to be 1.7 kg/L for columns with and without amendments. The retardation factors (R) for no amendment, 0.2% TOC and

0.2 % GAC were 28, 101 and $7x10^7$ respectively. Hydrodynamic conditions for GAC amended caps were assumed to be the same as non-amended caps.

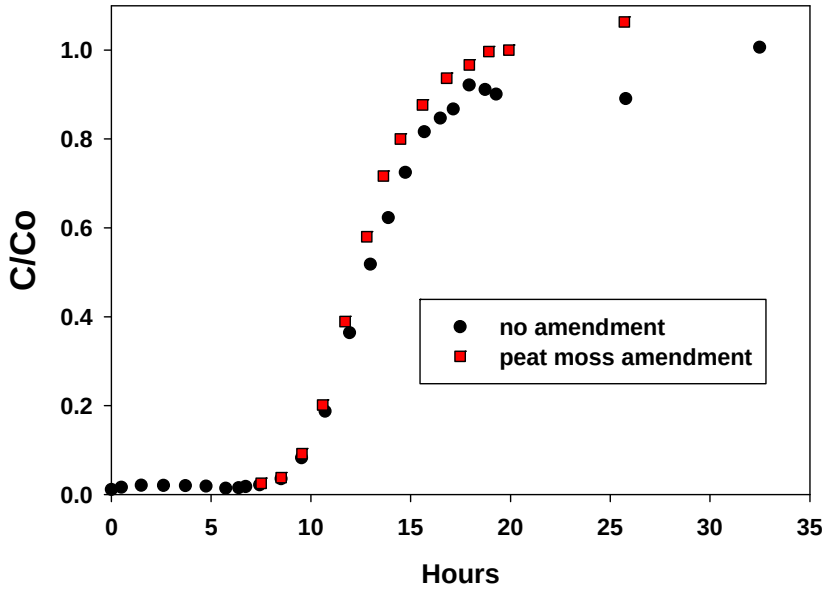


**Figure 18. Tracer study results of laboratory column experiment showing transition from DI water to $CaCl_2$ solution for capping material with no amendment and peat moss amendment.**

Figure 19 shows the spatial migration of pyrene in the columns compared to several model simulations. Experimental pyrene migration exceeds model predictions in both amended and non-amended caps when looking at the cap near the column outlet. Deviations between the experimental results and a model can be attributed to four factors: First, column construction advances the pyrene migration initially which is not captured by the model. Second, the influent pyrene concentration (sediment pore water from port 1) was not constant, but increased over the time range being modeled. The average sediment pyrene porewater concentration for each particular column (amended or non-amended) was used as a constant input in the Ogata-Banks analytical solution (generally all concentrations were within ±5 µg/L of the calculated average pyrene concentration). This model assumes a constant input of PAHs for all times (this is more problematic when measuring some of the other PAHs which had more source concentration changes due to dissolution processes). The experimental measurements of pyrene in the sediment layer was used as a fluctuating input to the advection-dispersion equations solved by CXTFIT software (Toride, N. et al. 1999) to model pyrene migration in the column capping material when equilibrium partitioning is the primary mechanism for retardation in the cap. The CXTFIT code using a constant input matched the Ogata and Banks solution closely (Figure 19). Third,

PAHs and other organic compounds present in the sediment porewater could compete for sorption, effectively reducing the apparent $K_d$ values (as seen in batch experiments for pyrene). Fouling from other organics present (e.g. humic acids) in sediment has been observed to reduce the effectiveness of PAH sorption in chars (Pignatello, J.J., et al., 2006). Fourth, the equilibrium partitioning assumption inherent in the calculation of the retardation factor may not be accurate due to the short fluid residence time in the column and possible existence of immobile zones within the column. This could be the case given a porosity of 0.47 (greater than 0.24 or 0.25 from tracer test) calculated from the specific gravity of the cap, bulk density of the cap, and the specific weight of water. The modeling utilized porosity measurements from the tracer studies. However, sorption sites trapped in immobile zones may have reduced the % TOC available to an effectively smaller TOC content.

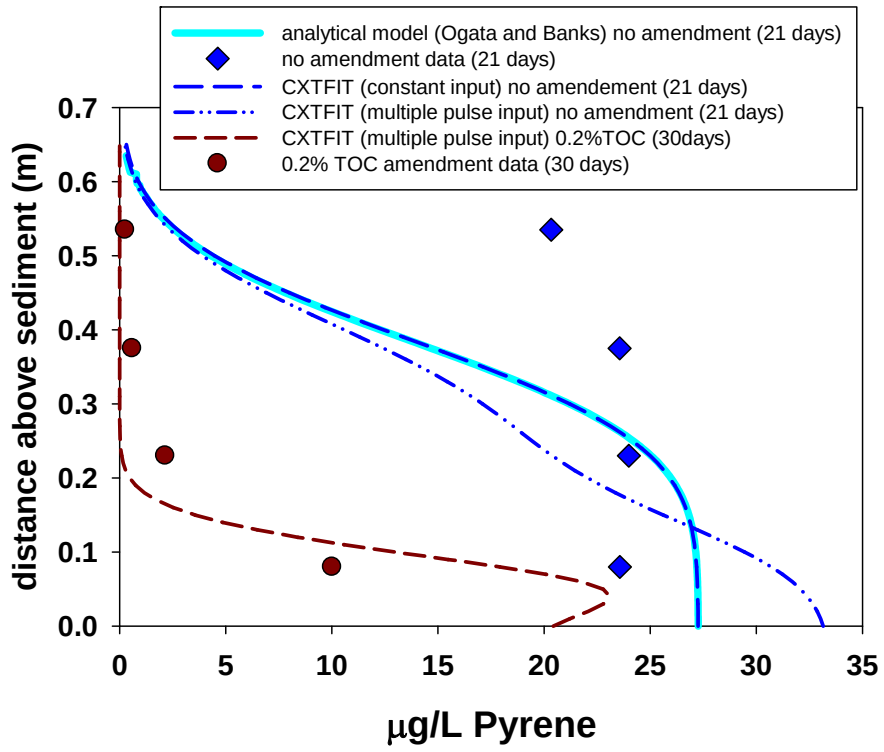


**Figure 19. Spatial Migration of Pyrene in Columns not amended and amended with 0.2% TOC with comparisons between analytical and CXTFIT models.**

The observed migration of phenanthrene though the capping material was modeled using the CXTFIT code. Figure 20 shows the temporal migration of phenanthrene in the columns compared to several model simulations. Experimental phenanthrene migration compared well with model predictions when contrasting the various capping treatments. The experimental measurements of phenanthrene in the sediment layer (port 1) was used as a fluctuating input to the advection-dispersion equations solved by CXTFIT software (Toride, N. et al. 1999) to model phenanthrene migration in the column capping material when equilibrium partitioning is the primary mechanism for retardation in the cap. Deviations between the experimental results and a model are attributed to three factors: First, due to the limited number of SPME collection points some of the concentration changes in the source zone may have been missed. Second, PAHs and other organic compounds present in the sediment porewater could compete for sorption, effectively reducing the apparent $K_d$ values. Fouling from other organics present (e.g. humic acids) in sediment has been observed to reduce the effectiveness of PAH sorption in chars (Pignatello, J.J., et al., 2006). Third, the equilibrium partitioning assumption inherent in the calculation of the retardation factor may not be accurate due to the short fluid residence time in the column and possible existence of immobile zones within the column.

The predicted concentration of PAHs in the GAC amended column was near zero and the measured aqueous concentrations were also close to or below the quantitation limits. As described earlier, none of the PAHs were seen to break through the GAC amended columns and this is what the model also predicted.

Modeling of biological systems showed that no noticeable degradation should be expected in the porewater of the columns during the short residence times operated in the experimental column. However, if a biofilm develops in the cap solids, biodegradation rates can compete with the rate of flushing. What is also likely to occur is an increased sorption of PAH to attached growth on the capping material in a biologically amended system. This is most likely the cause of the reduced phenanthrene concentrations in the biologically amended column compared to the model shown in Figure 20.

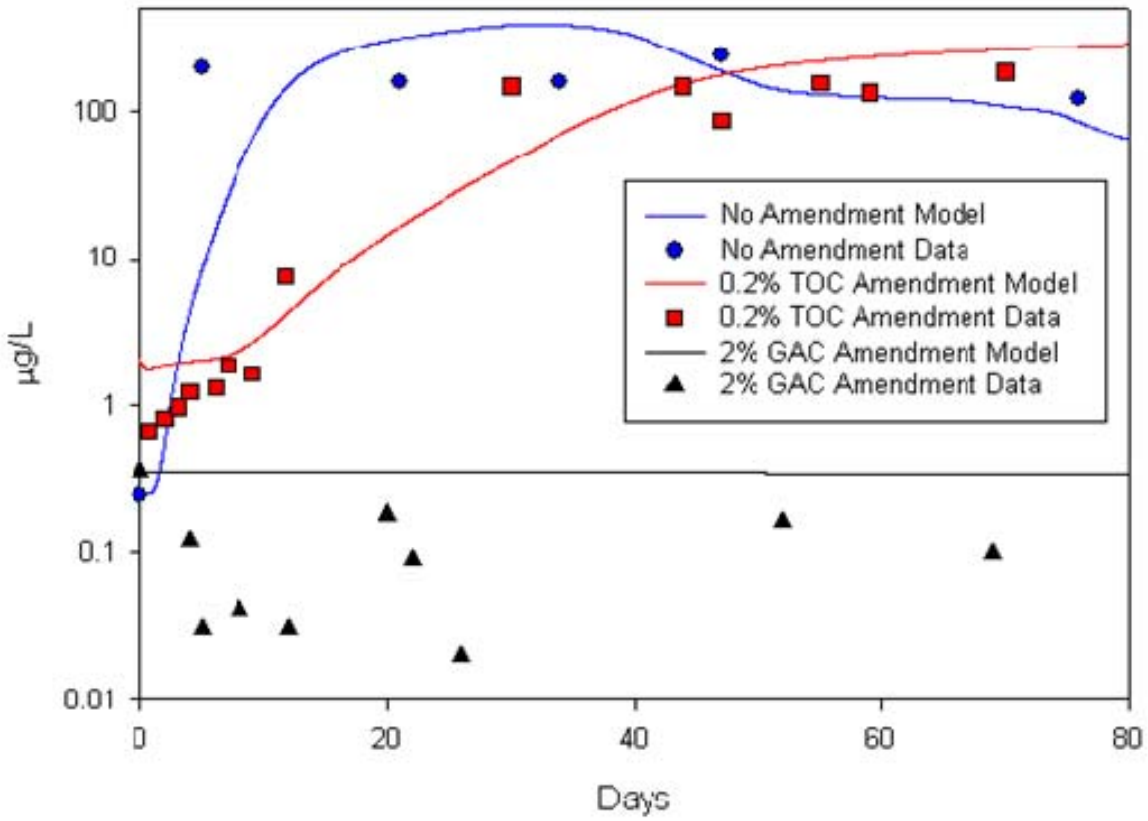


**Figure 20. Phenanthrene migration at Port 5 over time in non-amended, peat amended, and GAC amended columns and model predictions. The GAC data are below the limit of quantification for SPME.**

The impact of biodegradation on overall contaminant transport through a porous media is strongly influenced by the relative rates of degradation and advection. At high Darcy velocity, residence time is too short to observe a concentration decrease due to biodegradation. The column studies performed in the laboratory were operated at a Darcy velocity of 0.015 m/hr due to limitations with maintaining low flowrates through a column and also challenges with the length of time required to observe close to breakthough when flowrates are small. The transport model with parameters derived from laboratory experimental observations was used to perform simulations of biodegradation in the column operating at different Darcy velocities. As shown in Figure 21, breakthrough starts close to 20 bed volumes at a Darcy velocity of 0.015 m/hr and there is little difference between a biologically active and inactive column at this flow rate. The residence time is too short for biodegradation to have an

impact. When the Darcy velocity is reduced 100-fold to 0.00015 m/hr, the effect of biodegradation is more apparent. Thus, biodegradation will play a role in PAH retention within the cap when groundwater velocities are small and biodegradation rates are favorable compared to the flushing rate. Also, it is important to remember that the biodegradation modeling is limited to degradation by organisms present in the water phase. If an actively degrading biofilm develops on the cap solids over time, the effective biodegradation rates could be enhanced. However, this was not observed in the duration of laboratory column experiments.

Extending the model parameterized using experimental measurements we can simulate long-trerm performance of the columns. Shown in Figure 22 is a simulation of phenanthrene breakthrough in columns amended with peat moss (TOC of 0.2%, 0.5%, and 2%) and activated carbon (GAC of 0.002% and 0.2%). The input concentration to the cap is assumed to be constantat at 100 μg/K of dissolved phenanthrene. As illustrated in Figure 22, peat moss (a surrogate for natural organic matter) is much less effective in retarding phenanthrene compared to activated carbon. At 0.2% TOC in the form of peat moss in the cap, phenanthrene breakthrough takes place in a couple of months and with a higher dose of peat moss at 2% TOC, the breakthrough is delayed to 8 months. A very small dose of GAC (0.002%) breakthrough is delayed to 10 years and with 0.2% AC, the breakthrough is longer than 1000 years. These simulation results explain why the laboratory experiments with 0.2 and 2% GAC in the cap did not observe PAH breakthrough over 6 months of monitoring. It is possible that mass transfer limitations within carbon particles and fouling of the carbon with other organic molecules may degrade long-term performance to some extent. However, with the large reductions in PAH transport evident from the laboratory experiments and modeling simulations with GAC amended sand caps, it appears promising to include GAC amndments in sand caps to enhance performance where groundwater advection is of concern.

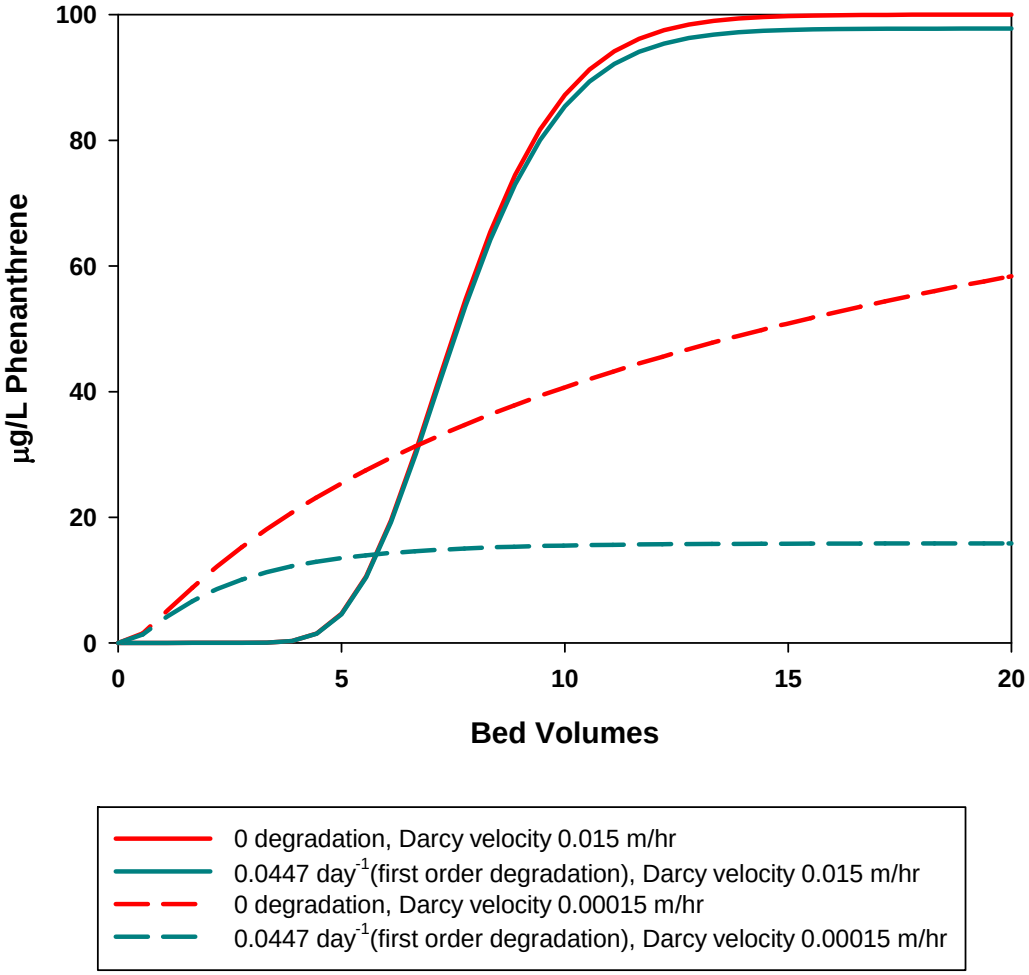


**Figure 21. Effect of Darcy velocity on biodegradation in cap**

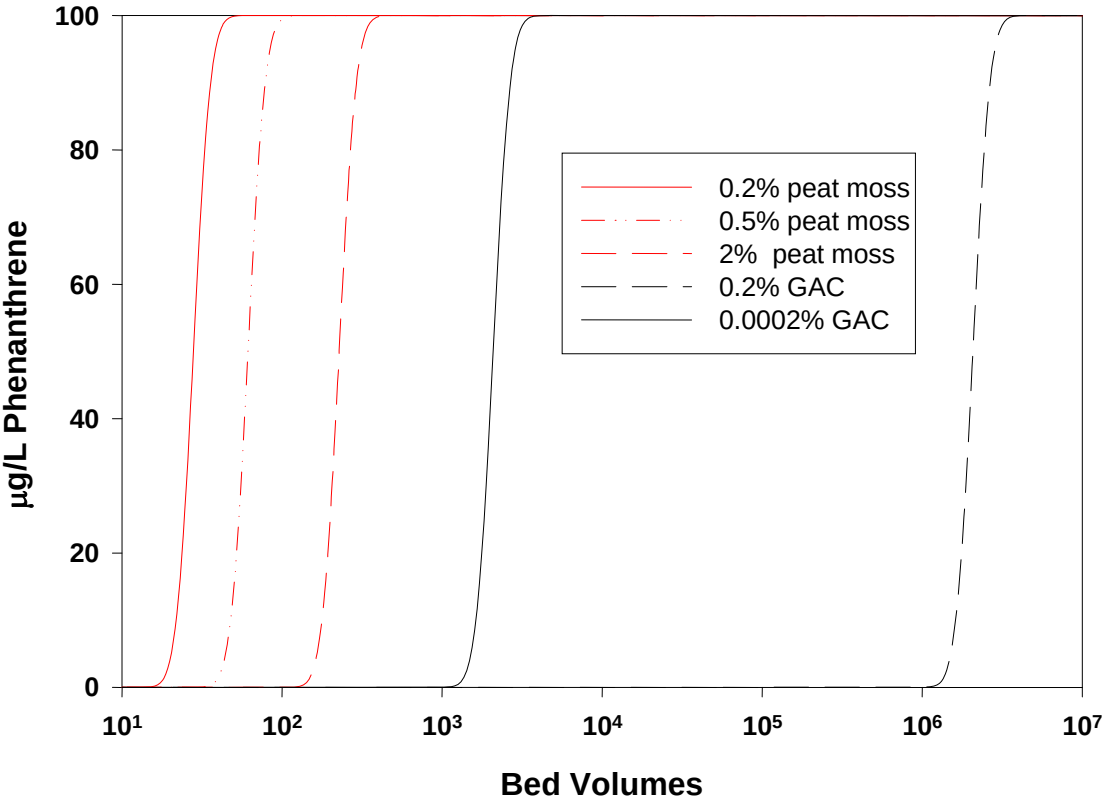


**Figure 22. Effect of peat moss and GAC amendment on breakthrough times of phenanthrene in sand cap.**

# VI. CONCLUSIONS AND RECOMMENDATIONS

**The main conclusions of this study are as follows:**

1) PAH dissolution of a creosote contaminated sediment can be described by Raoult's law
2) There is potential of PAH breakthrough in typical low organic carbon sand caps placed in the field when there is groundwater advection.
3) Amendment of sediment caps with natural organic matter in the form of peat moss is moderately successful in reducing PAH transport.
4) Amendment of sediment caps with activated carbon in the range of 0.2 – 2% by weight greatly reduces PAH transport through a sand cap.
5) The dissolution and transport of PAHs in a sand cap can be modeled in two phases: the first phase describing the time variant dissolution process from creosote and the second phase involving retarded transport through the capping amterial.
6) Measurement of PAH concentration in cores taken out of sediment caps is a poor indicator of contaminant breakthrough, especially in cases where there is little capacity in the cap material to bind contaminants.
7) Experiments with sediment caps with and without biological activity did not show remarkable difference for the flow conditions tested. It is possible that in the long-term over many years, a biological community in the form of biofilms may develop in the capping material that adds to the effectiveness of the cap in limiting contaminant migration.

**The main recommendations for future work based on this study are:**

1) The next step in the technology transition process should involve pilot-scale testing of amended sand caps placed over contaminated sediments at a site where groundwater flow has been documented. A long-term monitoring plan should evaluate migration of porewater contaminants through the cap over time for variously amended caps.
2) Additional laboratory-scale research is needed to develop efficient methods to deploy amendments to caps without having the sand and amendment segregate during placement under water due to density differences. Delivery of amendments through specially manufactured pellets such as SediMite™ (ESTCP project ER-0835) could be a viable option but needs to be tested. The sorbents could be delivered to achieve an uniform distribution within the cap or as a distinct layer within the cap. Engineering feasibility and effectiveness of either approach needs to be tested in the field.

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# VII. LIST OF PUBLICATIONS

**List of Papers**

Paper 1: SPME Measurement of Porewater PAH Transport in Amended Sediment Caps

Philip Gidley, Seokjoon Kwon, and Upal Ghosh (in preparation)

**List of Posters/Presentations**

1. Characterization of Contaminant Transport Through In-Place Sediment Caps-Poster

P. Gidley, L. Lockard, S. Kwon, U. Ghosh

29th Annual Graduate Research Conference

University of Maryland Baltimore County, Baltimore, MD 4-24-07

2. Characterization of Contaminant Transport Through In-Place Sediment Caps-Poster

P. Gidley, L. Lockard, S. Kwon, U. Ghosh

Society of Environmental Toxicology and Chemistry (SETAC), Chesapeake and Potomac Regional Chapter Meeting

Laurel, MD 4-07

3. Measurement of Porewater PAH Transport in Sediment Caps using Solid-phase Microextraction(SPME)-Presentation

P. Gidley, S. Kwon, U. Ghosh

Connecting people-Linking the fundamental concepts of sediment pollution remediation and ecotoxicity for improved engineering designs

Newcastle University, Newcastle, England 11-2-07

4. SPME measurement of porewater PAH transport in amended sediment caps-Presentation

P. Gidley, S. Kwon, U. Ghosh

SETAC North America 28th Annual Meeting

Milwaukee, WI 11-18-07

5. Characterization of Contaminant Transport through In-Place Sediment Caps-Poster

P. Gidley, S. Kwon, U. Ghosh

Gordon Research Conference, Environmental Sciences: Water

Holderness, NH 6-25-08

6. SPME measurement of porewater PAH transport in amended sediment caps-Presentation

P. Gidley, S. Kwon, U. Ghosh

SETAC North America 29th Annual Meeting

Tampa, FL 11-18-08

7. Porewater PAH transport in amended sediment caps-Poster

P. Gidley, S. Kwon, U. Ghosh

American Geophysical Union (AGU) meeting

Toronto, ON 5-22-09

8. Modeling and SPME measurement of porewater PAH transport in amended sediment caps-Poster

P. Gidley, N. Agarwal, S. Kwon, and U. Ghosh

Strategic Environmental Research and Development Program (SERDP), Partners in Environmental Technology Technical Symposium & Workshop

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APPENDIX 1. Table of data used in Figures.

Figure 3. (with some additional information)

| | Sediment After Mixing Before Sieving | | Sediment After Sieving | | Capping Material | |
|---|---|---|---|---|---|---|
| | ug/g | StDev | ug/g | StDev | ug/g | StDev |
| Naphthalene | 16.2 | 9.1 | 4.8 | 1.3 | 0.002 | 0.0006 |
| Acenaphthylene | 14.2 | 1.5 | 6.8 | 1.3 | 0.001 | 0.0001 |
| Acenaphthene | 162.0 | 19.8 | 110.0 | 16.6 | 0.001 | 0.0003 |
| Fluorene | 76.2 | 9.3 | 53.4 | 7.3 | 0.001 | 0.0003 |
| Phenanthrene | 268.6 | 30.0 | 194.4 | 25.0 | 0.005 | 0.0013 |
| Anthracene | 64.4 | 11.6 | 114.2 | 7.2 | 0.005 | 0.0008 |
| Fluoranthene | 221.9 | 26.5 | 163.5 | 15.5 | 0.030 | 0.0071 |
| Pyrene | 152.5 | 18.2 | 128.0 | 27.2 | 0.019 | 0.0040 |
| Benz(a)anthracene | 30.7 | 3.4 | 22.0 | 2.5 | 0.009 | 0.0013 |
| Chrysene | 23.0 | 3.2 | 27.7 | 6.1 | 0.010 | 0.0024 |
| Benzo(b)fluoranthene | 10.1 | 0.9 | 6.9 | 2.5 | 0.005 | 0.0001 |
| Benzo(k)fluoranthene | 8.4 | 1.0 | 5.7 | 1.3 | 0.004 | 0.0000 |
| Benzo(a)pyrene | 8.3 | 1.0 | 5.5 | 1.1 | 0.004 | 0.0005 |
| Indeno(1,2,3-cd)pyrene | 1.7 | 0.3 | 1.1 | 0.1 | 0.002 | 0.0001 |
| Dibenz(a,h)anthracene | 1.3 | 1.2 | 0.5 | 0.0 | 0.000 | 0.0001 |
| Benzo(g,h,i)perylene | 2.9 | 2.4 | 1.2 | 0.1 | 0.001 | 0.0000 |
| | | | | | | |
| Totals | 1062 | | 846 | | 0.098 | |

Figure 4.

| | Eq aqueous PAH conc, ug/L | |
|---|---|---|
| | **Sieved** | **Bulk** |
| Acenaphthylene | 320.14 | 341.61 |
| Acenaphthene | 5194.19 | 5373.34 |
| Fluorene | 1508.61 | 1435.41 |
| Phenanthrene | 2467.44 | 2013.79 |
| Anthracene | 343.64 | 290.57 |
| Fluoranthene | 484.29 | 359.37 |
| Pyrene | 268.49 | 196.38 |
| Benz(a)anthracene | 13.96 | 10.57 |
| Chrysene | 13.79 | 10.15 |
| Benzo(b)fluoranthene | 2.82 | 2.16 |
| Benzo(k)fluoranthene | 1.92 | 1.29 |
| Benzo(a)pyrene | 1.72 | 1.42 |
| Indeno(1,2,3-cd)pyrene | 0.00 | 0.51 |
| Dibenz(a,h)anthracene | 0.00 | 0.00 |
| Benzo(g,h,i)perylene | 0.00 | 0 |

Figure 5.

| | Log($K_{TOC}$) Sieved | Log($K_{TOC}$) Bulk | Log($K_{TOC}$) Lit values |
|---|---|---|---|
| Acenaphthylene | 4.81 | 4.68 | - |
| Acenaphthene | 4.63 | 4.68 | - |
| Fluorene | 4.93 | 4.97 | - |
| Phenanthrene | 5.38 | 5.37 | 5.6 |
| Anthracene | 5.62 | 6.02 | 5.8 |
| Fluoranthene | 6.07 | 6.03 | 6 |
| Pyrene | 6.17 | 5.68 | 5.9 |
| Benz(a)anthracene | 6.76 | 6.71 | 6.9 |
| Chrysene | 6.64 | 6.81 | 6.8 |
| Benzo(b)fluoranthene | 6.99 | 6.90 | 7.4 |
| Benzo(k)fluoranthene | 7.15 | 6.98 | 7.4 |
| Benzo(a)pyrene | 7.06 | 7.02 | 7.15 |

Figure 6a.

**PAH profile through the Column 2 Dec 21, 2006** Out of linear range

calibration range

| | | Port | 1 | 2 | 3 | 4 | 5 | 6 | |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 5.5-1106.6 | | 23.51 | 114.19 | 2.38 | | | | ug/L |
| Acenaphthylene | 1.2-240.4 | | 31.08 | 14.62 | 2.05 | 0.03 | | | ug/L |
| Acenaphthene | 1.4-293.7 | | 641.82 | 268 | 41.16 | 0.07 | | | ug/L |
| Fluorene | 1.0-201.4 | | 180.14 | 72.26 | 16.48 | 0.04 | 0.03 | | ug/L |
| Phenanthrene | 0.73-146.8 | | 207.61 | 60.28 | 12.46 | 0.26 | 0.24 | | ug/L |
| Anthracene | 0.8-16 | | 30.48 | 7.26 | 1.76 | 0.09 | 0.07 | | ug/L |
| Fluoranthene | 0.28-56.4 | | 59.29 | 4.59 | 1.08 | 0.24 | 0.26 | | ug/L |
| Pyrene | 0.24-48 | | 39.03 | 2.64 | 0.59 | 0.18 | 0.18 | | ug/L |
| Benzo(a)anthracene | 0.01-2.2 | | 11.92138 | 0.62306 | 0.04803 | | | | ug/L |
| Chrysene | 0.004-0.8 | | 5.98609 | 0.35727 | 0.03453 | 0.02182 | | | ug/L |

Figure 6b.

**PAH profile through the Column 2 Dec 26, 2006** Out of linear range

linear range

| | | Port | 1 | 2 | 3 | 5 | 6 | |
|---|---|---|---|---|---|---|---|---|
| Naphthalene | 5.5-1106.6 | | 11.02 | 42.18 | 76.84 | 86.87 | 86.29 | ug/L |
| Acenaphthylene | 1.2-240.4 | | 43.47 | 49.44 | 40.96 | 51.31 | 38.59 | ug/L |
| Acenaphthene | 1.4-293.7 | | 922.1 | 932.76 | 732.32 | 1034.46 | 765.36 | ug/L |
| Fluorene | 1.0-201.4 | | 270.34 | 244.93 | 206.24 | 228.89 | 207.24 | ug/L |
| Phenanthrene | 0.73-146.8 | | 282.51 | 244.7 | 212.06 | 196.14 | 219.74 | ug/L |
| Anthracene | 0.8-16 | | 36.88 | 34.5 | 30.15 | 26.88 | 29.53 | ug/L |
| Fluoranthene | 0.28-56.4 | | 37.48 | 22.16 | 23.12 | 10.64 | 17.03 | ug/L |
| Pyrene | 0.24-48 | | 19.84 | 10.89 | 11.17 | 4.84 | 7.34 | ug/L |
| Benzo(a)anthracene | 0.01-2.2 | | 0.46855 | 0.13196 | 0.07789 | 0.03981 | 0.07228 | ug/L |
| Chrysene | 0.004-0.8 | | 0.37632 | 0.13112 | 0.10148 | 0.06538 | 0.12311 | ug/L |

Figure 7 (with details of each core)

| DEPTH | TR1 00 A | TR1 10 A | TR1 20 A | TR1 20 A C2 | TR1 40 A | TR4 00 A | TR4 -10 A | TR4 20 A | TR4 40A | TR5 00 A | TR5 20 A | Koc foc predictions Lab column | Extractions Lab column |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 1173 | | | | | | | | | | | | |
| 7 | 694 | | | | | | | | | | | | |
| 62.5 | | 2315 | | | | | | | | | | | |
| 58 | | 2581 | | | | | | | | | | | |
| 54 | | 3283 | | | | | | | | | | | |
| 50 | | 1911 | | | | | | | | | | | |
| 46 | | 4176 | | | | | | | | | | | |
| 42 | | 4032 | | | | | | | | | | | |
| 38 | | 4848 | | | | | | | | | | | |
| 34 | | 7130 | | | | | | | | | | | |
| 30 | | 19786 | | | | | | | | | | | |
| 26 | | 16527 | | | | | | | | | | | |
| 22 | | 5619 | | | | | | | | | | | |
| 19 | | 14114 | | | | | | | | | | | |
| 17 | | 4342 | | | | | | | | | | | |
| 15 | | 1247 | | | | | | | | | | | |
| 13 | | 867 | | | | | | | | | | | |
| 11 | | 1292 | | | | | | | | | | | |
| 9 | | 727 | | | | | | | | | | | |
| 7 | | 1199 | | | | | | | | | | | |
| 5 | | 1081 | | | | | | | | | | | |
| 3 | | 1269 | | | | | | | | | | | |
| 1 | | 4734 | | | | | | | | | | | |
| 78 | | | 1045 | | | | | | | | | | |
| 58 | | | 902 | | | | | | | | | | |
| 54 | | | 441 | | | | | | | | | | |
| 46 | | | 163 | | | | | | | | | | |
| 38 | | | 27 | | | | | | | | | | |
| 34 | | | 13 | | | | | | | | | | |
| 30 | | | 7 | | | | | | | | | | |
| 26 | | | 8 | | | | | | | | | | |
| 22 | | | 8 | | | | | | | | | | |
| 19 | | | 29 | | | | | | | | | | |
| 17 | | | 4 | | | | | | | | | | |
| 13 | | | 7 | | | | | | | | | | |
| 11 | | | 7 | | | | | | | | | | |
| 7 | | | 26 | | | | | | | | | | |
| 3 | | | 61 | | | | | | | | | | |
| 67.5 | | | | 563 | | | | | | | | | |
| 58 | | | | 3558 | | | | | | | | | |
| 50 | | | | 163 | | | | | | | | | |
| 42 | | | | 133 | | | | | | | | | |
| 34 | | | | 35 | | | | | | | | | |
| 26 | | | | 7 | | | | | | | | | |
| 19 | | | | 21 | | | | | | | | | |
| 15 | | | | 11 | | | | | | | | | |
| 11 | | | | 10 | | | | | | | | | |
| 7 | | | | 137 | | | | | | | | | |
| 3 | | | | 318 | | | | | | | | | |
| 175 | | | | | 815 | | | | | | | | |
| 155 | | | | | 638 | | | | | | | | |
| 135 | | | | | 258 | | | | | | | | |
| 115 | | | | | 900 | | | | | | | | |
| 97.5 | | | | | 5535 | | | | | | | | |
| 87.5 | | | | | 94 | | | | | | | | |
| 77.5 | | | | | 66 | | | | | | | | |
| 67.5 | | | | | 25 | | | | | | | | |
| 58 | | | | | 16 | | | | | | | | |
| 50 | | | | | 5 | | | | | | | | |
| 42 | | | | | 25 | | | | | | | | |
| 34 | | | | | 76 | | | | | | | | |
| 26 | | | | | 40 | | | | | | | | |
| 19 | | | | | 47 | | | | | | | | |
| 15 | | | | | 45 | | | | | | | | |
| 11 | | | | | 27 | | | | | | | | |
| 7 | | | | | 60 | | | | | | | | |
| 3 | | | | | 67 | | | | | | | | |
| 50 | | | | | | 3151 | | | | | | | |
| 42 | | | | | | 229 | | | | | | | |
| 34 | | | | | | 145 | | | | | | | |
| 26 | | | | | | 37 | | | | | | | |
| 19 | | | | | | 68 | | | | | | | |
| 15 | | | | | | 59 | | | | | | | |
| 11 | | | | | | 65 | | | | | | | |
| 7 | | | | | | 105 | | | | | | | |
| 3 | | | | | | 297 | | | | | | | |
| 77.5 | | | | | | | 317 | | | | | | |
| 67.5 | | | | | | | 108 | | | | | | |
| 58 | | | | | | | 32 | | | | | | |
| 50 | | | | | | | 8 | | | | | | |
| 42 | | | | | | | 20 | | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 34 | 8 | | | | | | | | |
| 26 | 14 | | | | | | | | |
| 19 | 17 | | | | | | | | |
| 15 | 8 | | | | | | | | |
| 11 | 25 | | | | | | | | |
| 7 | 451 | | | | | | | | |
| 3 | 812 | | | | | | | | |
| | | | | | | | | | |
| 155 | | 996 | | | | | | | |
| 135 | | 482 | | | | | | | |
| 115 | | 522 | | | | | | | |
| 97.5 | | 251 | | | | | | | |
| 87.5 | | 279 | | | | | | | |
| 77.5 | | 112 | | | | | | | |
| 67.5 | | 55 | | | | | | | |
| 58 | | 8 | | | | | | | |
| 50 | | 26 | | | | | | | |
| 42 | | 29 | | | | | | | |
| 34 | | 11 | | | | | | | |
| 26 | | 7 | | | | | | | |
| 19 | | 8 | | | | | | | |
| 15 | | 24 | | | | | | | |
| 11 | | 24 | | | | | | | |
| 7 | | 92 | | | | | | | |
| 3 | | 726 | | | | | | | |
| | | | | | | | | | |
| 175 | | | 794 | | | | | | |
| 155 | | | 43 | | | | | | |
| 135 | | | 90 | | | | | | |
| 115 | | | 58 | | | | | | |
| 97.5 | | | 158 | | | | | | |
| 87.5 | | | 14 | | | | | | |
| 77.5 | | | 0 | | | | | | |
| 67.5 | | | 3 | | | | | | |
| 58 | | | 2 | | | | | | |
| 50 | | | 1 | | | | | | |
| 42 | | | 2 | | | | | | |
| 34 | | | 0 | | | | | | |
| 26 | | | 2 | | | | | | |
| 19 | | | 4 | | | | | | |
| 15 | | | 3 | | | | | | |
| 11 | | | 2 | | | | | | |
| 7 | | | 14 | | | | | | |
| 3 | | | 115 | | | | | | |
| | | | | | | | | | |
| 97.5 | | | | 314 | | | | | |
| 87.5 | | | | 191 | | | | | |
| 77.5 | | | | 1171 | | | | | |
| 67.5 | | | | 28 | | | | | |
| 58 | | | | 13 | | | | | |
| 50 | | | | 34 | | | | | |
| 42 | | | | 1 | | | | | |
| 34 | | | | 8 | | | | | |
| 26 | | | | 10 | | | | | |
| 19 | | | | 1921 | | | | | |
| 15 | | | | 1355 | | | | | |
| 11 | | | | 2499 | | | | | |
| 7 | | | | 3503 | | | | | |
| 3 | | | | 2103 | | | | | |
| | | | | | | | | | |
| 87.5 | | | | | 627 | | | | |
| 77.5 | | | | | 235 | | | | |
| 67.5 | | | | | 1576 | | | | |
| 58 | | | | | 1062 | | | | |
| 50 | | | | | 6838 | | | | |
| 42 | | | | | 6582 | | | | |
| 34 | | | | | 243 | | | | |
| 26 | | | | | 81 | | | | |
| 19 | | | | | 43 | | | | |
| 15 | | | | | 11 | | | | |
| 11 | | | | | 6 | | | | |
| 7 | | | | | 14 | | | | |
| 3 | | | | | 610 | | | | |
| Depth from Sediment | | | | | | | | | |
| 5 | | | | | | 2738 | | | |
| 25 | | | | | | 4236 | | | |
| 40 | | | | | | 4483 | | | |
| 45 | | | | | | 4392 | | | |
| 60 | | | | | | 3992 | | | |
| | | | | | | | | | |
| 57.15 | | | | | | | 1474 | | |
| 49.53 | | | | | | | 1806 | | |
| 41.91 | | | | | | | 4266 | | |
| 34.29 | | | | | | | 2819 | | |
| 19.05 | | | | | | | 6977 | | |
| 11.43 | | | | | | | 5492 | | |

Figure 8a.

**PAH profile through Column 6 July 24, 2007 8:30 am**

Out of calibration range low

Out of calibration range high

| | calibration range | Port | 1 | 2 | 3 | 4 | 5 | 6 | Units |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 5.5-2213.33 | | 37.4 | 19.68 | 6.74 | 6.95 | 2.82 | 1.87 | ug/L |
| Acenaphthylene | 1.2-481.06 | | 44.8 | 33.73 | 5.82 | 2.37 | 0.49 | 0.36 | ug/L |
| Acenaphthene | 1.4-586.67 | | 542.1 | 371.63 | 53.54 | 20.99 | 3.5 | 1.55 | ug/L |
| Fluorene | 1.0-402.67 | | 144.19 | 102.86 | 14.25 | 3.77 | 0.76 | 0.36 | ug/L |
| Phenanthrene | 0.73-293.33 | | 154.6 | 108.44 | 18.45 | 2.81 | 0.66 | 0.45 | ug/L |
| Anthracene | 0.8-32 | | 15.97 | 11.94 | 2.27 | 0.43 | 0.13 | 0.13 | ug/L |
| Fluoranthene | 0.28-112.53 | | 22.52 | 13.71 | 2.41 | 0.25 | 0.13 | 0.29 | ug/L |
| Pyrene | 0.24-96 | | 11.27 | 6.65 | 1.15 | 0.16 | 0.1 | 0.23 | ug/L |
| Benzo(a)anthracene | 0.01-4.27 | | 0.18319 | 0.20591 | 0.04109 | | | 0.06174 | ug/L |
| Chrysene | 0.004-1.6 | | 0.14912 | 0.16345 | 0.05495 | | | 0.04087 | ug/L |

figure 8b.

**PAH profile through Column 6 July 29, 2007 4:30 pm**

Out of calibration range low

Out of calibration range high

| | calibration range | Port | 1 | 2 | 3 | 4 | 5 | 6 | Units |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 5.5-2213.33 | | 9.34 | 18.21 | 20.75 | 21.58 | 40.21 | 25.91 | ug/L |
| Acenaphthylene | 1.2-481.06 | | 47.88 | 54.35 | 24.15 | 10.77 | 10.33 | 6.56 | ug/L |
| Acenaphthene | 1.4-586.67 | | 364.8 | 428.75 | 296.35 | 135.37 | 124.31 | 43.15 | ug/L |
| Fluorene | 1.0-402.67 | | 128.2 | 131.61 | 64.96 | 25.97 | 12.75 | 3.94 | ug/L |
| Phenanthrene | 0.73-293.33 | | 148.25 | 119.56 | 20.83 | 2.14 | 1.3 | 0.51 | ug/L |
| Anthracene | 0.8-32 | | 19.37 | 15.51 | 2.69 | 0.53 | 0.24 | 0.08 | ug/L |
| Fluoranthene | 0.28-112.53 | | 28.32 | 24.04 | 2.67 | 0.32 | 0.24 | 0.24 | ug/L |
| Pyrene | 0.24-96 | | 14.8 | 11.94 | 1.31 | 0.18 | 0.15 | 0.18 | ug/L |
| Benzo(a)anthracene | 0.01-4.27 | | 0.33096 | 0.22243 | | | | | ug/L |
| Chrysene | 0.004-1.6 | | 0.3072 | 0.2145 | | | | | ug/L |

Data for Initial PAH profile in 2% AC amended cap. (data in figure 9a is from a different time)

| **PAH profile through the Column 4 March 1, 2007** | | | **Low** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | calibration range | | **High** | | | | | | |
| | | **Port** | **1** | **2** | **3** | **4** | **5** | **6** | **Units** |
| Naphthalene | 5.5-2213.33 | | 261.38 | 4.11 | 1.16 | | 0.75 | 0.03 | ug/L |
| Acenaphthylene | 1.2-481.06 | | 39.62 | 0.35 | 0.09 | | 0.04 | 0 | ug/L |
| Acenaphthene | 1.4-586.67 | | 662.31 | 8.29 | 1.71 | | 0.58 | 0.02 | ug/L |
| Fluorene | 1.0-402.67 | | 122.61 | 2.01 | 0.51 | | 0.2 | 0.01 | ug/L |
| Phenanthrene | 0.73-293.33 | | 27.14 | 1.41 | 0.67 | | 0.36 | 0.04 | ug/L |
| Anthracene | 0.8-32 | | 2.18 | 0.26 | 0.07 | | 0.04 | 0 | ug/L |
| Fluoranthene | 0.28-112.53 | | 1.22 | 1.37 | 0.14 | | 0.06 | 0.01 | ug/L |
| Pyrene | 0.24-96 | | 0.78 | 0.99 | 0.09 | | 0.04 | 0.01 | ug/L |
| Benzo(a)anthracene | 0.01-4.27 | | 0.25794 | 0.44811 | 0.02353 | | 0.02486 | | ug/L |
| Chrysene | 0.004-1.6 | | 0.18943 | 0.30304 | 0.0317 | | 0.02257 | 0.00222 | ug/L |

figure 9b.

| **PAH profile through Column 4 March 12 7:00pm, 2007** | | | | | | Out of calibration range low | | |
|---|---|---|---|---|---|---|---|---|
| | calibration range | | | | | Out of calibration range high | | **Units** |
| | | **Port** | **1** | **2** | **3** | **4** | **6** | ug/L |
| Naphthalene | 5.5-2213.33 | | 9.27 | 0.09 | 0.06 | 0.03 | 0.03 | ug/L |
| Acenaphthylene | 1.2-481.06 | | 21.57 | 0.06 | 0.03 | 0.02 | 0.01 | ug/L |
| Acenaphthene | 1.4-586.67 | | 320.03 | 0.23 | 0.1 | 0.04 | 0.03 | ug/L |
| Fluorene | 1.0-402.67 | | 96.55 | 0.08 | 0.04 | 0.02 | 0.01 | ug/L |
| Phenanthrene | 0.73-293.33 | | 118.93 | 0.3 | 0.14 | 0.06 | 0.03 | ug/L |
| Anthracene | 0.8-32 | | 33 | 0.07 | 0.02 | 0.01 | 0.01 | ug/L |
| Fluoranthene | 0.28-112.53 | | 48.54 | 0.27 | 0.07 | 0.03 | 0.02 | ug/L |
| Pyrene | 0.24-96 | | 27.39 | 0.19 | 0.04 | 0.02 | 0.02 | ug/L |
| Benzo(a)anthracene | 0.01-4.27 | | 0.63669 | 0.04873 | 0.00783 | 0.00372 | 0.0064 | ug/L |
| Chrysene | 0.004-1.6 | | 0.42989 | 0.04411 | 0.0051 | 0.00251 | 0.00414 | ug/L |

Figure 10 (calculation of bed volumes needs to be updated slightly)

| No Amendment (Bed Volumes) | ug/L Phen Port 1 | ug/L Phen Port 6 | ug/L CHR Port 1 | ug/L CHR Port 6 |
|---|---|---|---|---|
| 0 | 207.61 | | 5.98 | |
| 9.0742 | 282.51 | 219.74 | 0.3563 | 0.1231 |
| 38.1118 | 403.98 | 122.05 | 0.653 | 0.181 |
| 61.7049 | 146.78 | 144.28 | 0.884 | 0.198 |
| 85.2979 | 126.52 | 242.65 | 0.889 | 0.2252 |
| 137.9285 | 37.18 | 112.1 | 1.337 | 0.4044 |
| | | | | |
| **0.2 % Peat Amendment (BV)** | | | | |
| 0 | 138.61 | | 0.288 | |
| 1.5047 | 154.6 | 0.45 | 0.149 | 0.041 |
| 3.9084 | 163.7 | 0.39 | 0.148 | 0.028 |
| 5.8627 | 173 | 0.41 | 0.203 | |
| 7.8169 | 214.34 | 0.64 | 0.375 | 0.065 |
| 11.9207 | 148.25 | 0.51 | 0.307 | |
| 13.875 | 237.75 | 0.71 | 0.464 | |
| 17.588 | 232.83 | 1.02 | 0.413 | |
| 23.0598 | 277.94 | 2.91 | 0.563 | |
| 58.6266 | 191.55 | 18.69 | 0.448 | 0.025 |
| 85.9857 | 311 | 71.01 | 0.921 | 0.018 |
| 91.8484 | 222.26 | 71.45 | 0.88 | 0.013 |
| 107.4821 | 448.64 | 126.74 | 1.48 | 0.015 |
| 115.299 | 267.62 | 115 | 1.13 | 0.019 |
| 136.7954 | 195.08 | 165.8 | 0.889 | 0.01 |

figure 11 (calculation of bed volumns needs to be corrected slightly)

| GAC 0.2% Bed Volumes | ug/L Phen Port 1 | ug/L Phen Port 6 | ug/L CHR Port 1 | ug/L CHR Port 6 |
|---|---|---|---|---|
| 0.1911 | 260.86 | 0.39 | 0.526 | 0.012 |
| 1.9108 | 237.3 | 0.49 | 0.394 | |
| 3.8216 | 366.8 | 0.51 | 1.875 | |
| 116.9406 | 4.41 | 0.09 | 0.45 | 7.00E-03 |
| | | | | |
| **GAC 2% Bed Volumns** | | | | |
| 0 | 27.14 | 0.04 | 0.1894 | 2.22E-03 |
| 5.1591 | 105.33 | 0.07 | | |
| 7.8343 | 255.93 | 0.04 | | |
| 13.5666 | 125.28 | 0.04 | 0.2854 | 4.98E-03 |
| 21.4009 | 118.93 | 0.03 | 0.4298 | 4.14E-03 |
| 36.3051 | 279.85 | 0.16 | 0.6908 | 0.01 |
| 40.3177 | 215.03 | 0.09 | 0.4825 | 2.57E-03 |
| 58.8524 | 150.12 | 0.02 | 0.303 | 1.50E-03 |
| 91.33 | 233.78 | 0.1 | 1.122 | |
| 391.7127 | 2.31 | 0.08 | 1.415 | 0.014 |

Figure 12

| NPH ug/L | ACY ug/L | ACE ug/L | FLR ug/L | PHN ug/L | ANTH ug/L | FLN ug/L | PYR ug/L | BaA ug/L | CHR ug/L | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2.44 | 3.58 | 108.74 | 37.37 | 46.87 | 13.09 | 51.16 | 29.32 | 1.17 | 1.01 | **Sieved EH Sediment (S:L Ratio 0.04)** |
| 2.01 | 3.44 | 109.44 | 37.11 | 45.92 | 12.66 | 49.58 | 27.97 | 0.92 | 0.84 | **Sieved EH Sediment (S:L Ratio 0.04)** |
| 1.47 | 2.49 | 96.62 | 28.4 | 31.43 | 10.36 | 37.59 | 20.96 | 0.69 | 0.61 | **Sieved EH Sediment (S:L Ratio 0.04)** |
| 1.33 | 1.82 | 88.13 | 26.52 | 29.39 | 9.71 | 35.1 | 20.13 | 0.64 | 0.58 | **Sieved EH Sediment (S:L Ratio 0.04)** |
| 1.99 | 0.19 | 2.34 | 1.65 | 22.48 | 8.27 | 42.55 | 25.07 | 2.07 | 1.28 | **Column run 4 months (S:L Ratio 0.04)** |
| 1.94 | 0.17 | 2.34 | 1.66 | 22.12 | 7.9 | 39.66 | 23.24 | 1.34 | 0.94 | **Column run 4 months (S:L Ratio 0.04)** |
| 1.36 | 0.15 | 2.12 | 1.34 | 15.54 | 6.78 | 31.81 | 18.62 | 1.2 | 0.79 | **Column run 4 months (S:L Ratio 0.04)** |
| 1.19 | 0.06 | 1.86 | 1.16 | 13.61 | 5.71 | 28.58 | 17.08 | 1.38 | 0.88 | **Column run 4 months (S:L Ratio 0.04)** |
| 1.72 | 0.12 | 1.08 | 0.43 | 2.22 | 2.05 | 40.17 | 25.77 | 2.4 | 1.36 | **Column run 7 months (S:L Ratio 0.04)** |
| 1.68 | 0.11 | 0.97 | 0.39 | 2.04 | 1.69 | 35.39 | 22.79 | 1.61 | 1.05 | **Column run 7 months (S:L Ratio 0.04)** |
| 1.17 | 0.09 | 0.93 | 0.32 | 1.45 | 1.5 | 29.18 | 18.56 | 1.44 | 0.85 | **Column run 7 months (S:L Ratio 0.04)** |
| 1.16 | 0.11 | 0.93 | 0.32 | 1.47 | 1.51 | 29.51 | 19.04 | 1.66 | 1 | **Column run 7 months (S:L Ratio 0.04)** |

Figure 13

| | Initial | ug/L | 18 days | ug/L |
|---|---|---|---|---|
| **BOD Solution** | average | 0.733333 | average | 0.04 |
| | stdev | 0.051316 | stdev | 0.014142 |
| **BOD Solution (4xspike)** | average | 2.936667 | average | 0.045 |
| | stdev | 0.090738 | stdev | 0.007071 |
| **BOD with NaN3** | average | 0.983333 | average | 0.25 |
| | stdev | 0.032146 | stdev | 0.042426 |
| **My Nutrient Mix** | average | 1.246667 | average | 0.045 |
| | stdev | 0.046188 | stdev | 0.007071 |

Figure 14

| Days | ug/L Living | stdev | ug/L Killed | stdev |
|---|---|---|---|---|
| 0 | 286.57 | 18.89 | 472.11 | 18.52 |
| 4 | 98.46 | 0.73 | 134.28 | 10.06 |
| 10 | 0.11 | 0.02 | 81.35 | 6.00 |

Figure 15

| | Port 1 | Port 2 | Port 3 | Port 4 | Port 5 | |
|---|---|---|---|---|---|---|
| | Distance from Sediment | | | | | |
| **BV** | **1cm** | **16cm** | **31cm** | **46cm** | **61cm** | **Overlying Water** |
| 0 | 15.96 | 0.59 | 0.17 | 0.19 | 0.03 | |
| 0.9 | 42.29 | 9.84 | 3.29 | 0 | 0 | |
| 1.9 | 53.43 | 29.82 | 26.46 | 14.24 | 0.67 | |
| 8.1 | 10.42 | 7.58 | 4.66 | 0.54 | 0.06 | 3.95 |
| 15.5 | 1.91 | 10.39 | 26.17 | 24.59 | 16.15 | 4.56 |
| 21 | 1.01 | 1.34 | 14.41 | 15.15 | 11.26 | 0.58 |
| 24.7 | 0.77 | 0.8 | 13.71 | 12.63 | 6.43 | 10.87 |
| 37.9 | 0.77 | 0.13 | 0.79 | 0.73 | 0.49 | 1 |
| 63.1 | 0.39 | 0.09 | 0.07 | 0.05 | 0.06 | 0.46 |
| 90.7 | 0 | 2.51 | 0 | 0 | 0.05 | |

**Figure 18**

| No Amendment | |
|---|---|
| Minutes | Concentration (C/Co) |
| 0 | 0.0115 |
| 30 | 0.0166 |
| 90 | 0.021 |
| 156.9 | 0.0207 |
| 222.9 | 0.02 |
| 284.4 | 0.019 |
| 343.8 | 0.0142 |
| 382.8 | 0.0153 |
| 403.8 | 0.018 |
| 445.8 | 0.0217 |
| 510.3 | 0.0356 |
| 571.8 | 0.0827 |
| 642.9 | 0.1875 |
| 716.4 | 0.3641 |
| 778.8 | 0.518 |
| 832.8 | 0.6231 |
| 883.8 | 0.7247 |
| 940.8 | 0.8163 |
| 988.8 | 0.8468 |
| 1027.8 | 0.8671 |
| 1075.8 | 0.9214 |
| 1123.8 | 0.9112 |
| 1156.8 | 0.9101 |

| Peat Amendment | |
|---|---|
| Minutes | Concentration (C/Co) |
| 450.6 | 0.0253 |
| 510.6 | 0.0383 |
| 573 | 0.092 |
| 635.4 | 0.202 |
| 702.9 | 0.389 |
| 768 | 0.58 |
| 818.1 | 0.716 |
| 869.1 | 0.8 |
| 935.7 | 0.8766 |
| 1008.3 | 0.9367 |
| 1076.4 | 0.9667 |
| 1134.9 | 0.9967 |
| 1195.2 | 1 |

**Figure 20, 1st Biological Column Data and Model**
**CXTFIT**
degradation rate for these simulations = 0.0447 day $^{-1}$ (Based on Peters et al. 1999, ES&T, 33, 4499)

| model Bed Volume degradation | model [ug/L] degradation | data Bed Volume | data [ug/L] | model Bed Volume no degradation | model [ug/L] no degradation |
|---|---|---|---|---|---|
| 0 | 0.26 | 0 | 0.16 | 0 | 0.26 |
| 1.89 | 0.3761 | 0.87 | 0.13 | 1.89 | 0.3767 |
| 3.78 | 2.5313 | 1.89 | 0.74 | 3.78 | 2.5394 |
| 5.67 | 6.3412 | 8.1 | 0.13 | 5.67 | 6.3718 |
| 7.56 | 12.013 | 15.5 | 16.22 | 7.56 | 12.09 |
| 9.45 | 21.085 | 21 | 11.35 | 9.45 | 21.255 |
| 11.34 | 34.651 | 24.7 | 6.49 | 11.34 | 34.986 |
| 13.23 | 52.989 | 37.9 | 1.52 | 13.23 | 53.588 |
| 15.12 | 74.039 | | | 15.12 | 74.994 |
| 17.01 | 93.599 | | | 17.01 | 94.958 |
| 18.9 | 107.52 | | | 18.9 | 109.25 |
| 20.79 | 113.62 | | | 20.79 | 115.62 |
| 22.68 | 112.08 | | | 22.68 | 114.23 |
| 24.57 | 104.72 | | | 24.57 | 106.88 |
| 26.46 | 93.914 | | | 26.46 | 95.966 |
| 28.35 | 81.718 | | | 28.35 | 83.599 |
| 30.24 | 69.506 | | | 30.24 | 71.179 |
| 32.13 | 58.013 | | | 32.13 | 59.464 |
| 34.02 | 47.582 | | | 34.02 | 48.813 |
| 35.91 | 38.36 | | | 35.91 | 39.385 |
| 37.8 | 30.396 | | | 37.8 | 31.233 |

**Figure 21 (phenanthrene, constant input)**
**CXTFIT**

**Darcy velocity = 0.015 m/hr**

| Bed Volumes No Degradation | [ug/L] No Degradation | Bed Volumes Degradation | [ug/L] Degradation |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.5556 | 0 | 0.5556 | 0 |
| 1.1111 | 1.77E-17 | 1.1111 | 1.76E-17 |
| 1.6667 | 1.12E-09 | 1.6667 | 1.12E-09 |
| 2.2222 | 7.51E-06 | 2.2222 | 7.46E-06 |
| 2.7778 | 1.27E-03 | 2.7778 | 1.26E-03 |
| 3.3333 | 0.0337 | 3.3333 | 0.0334 |
| 3.8889 | 0.3124 | 3.8889 | 0.3091 |
| 4.4444 | 1.4963 | 4.4444 | 1.4787 |
| 5 | 4.6302 | 5 | 4.5699 |
| 5.5556 | 10.584 | 5.5556 | 10.433 |
| 6.1111 | 19.483 | 6.1111 | 19.183 |
| 6.6667 | 30.607 | 6.6667 | 30.103 |
| 7.2222 | 42.743 | 7.2222 | 41.998 |
| 7.7778 | 54.653 | 7.7778 | 53.653 |
| 8.3333 | 65.401 | 8.3333 | 64.154 |
| 8.8889 | 74.467 | 8.8889 | 72.998 |
| 9.4444 | 81.705 | 9.4444 | 80.048 |
| 10 | 87.228 | 10 | 85.417 |
| 10.5556 | 91.284 | 10.5556 | 89.355 |
| 11.1111 | 94.17 | 11.1111 | 92.153 |
| 11.6667 | 96.169 | 11.6667 | 94.087 |
| 12.2222 | 97.521 | 12.2222 | 95.393 |
| 12.7778 | 98.418 | 12.7778 | 96.258 |
| 13.3333 | 99.003 | 13.3333 | 96.821 |
| 13.8889 | 99.378 | 13.8889 | 97.182 |
| 14.4444 | 99.616 | 14.4444 | 97.411 |
| 15 | 99.765 | 15 | 97.553 |
| 15.5556 | 99.857 | 15.5556 | 97.642 |
| 16.1111 | 99.914 | 16.1111 | 97.696 |
| 16.6667 | 99.948 | 16.6667 | 97.729 |
| 17.2222 | 99.969 | 17.2222 | 97.748 |
| 17.7778 | 99.982 | 17.7778 | 97.76 |
| 18.3333 | 99.989 | 18.3333 | 97.767 |
| 18.8889 | 99.994 | 18.8889 | 97.772 |
| 19.4444 | 99.996 | 19.4444 | 97.774 |
| 20 | 99.998 | 20 | 97.776 |

**Darcy velocity = 0.00015 m/hr**

| Bed Volumes No Degradation | [ug/L] No Degradation | Bed Volumes Degradation | [ug/L] Degradation |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.5539 | 1.5215 | 0.5539 | 1.3569 |
| 1.1077 | 5.1481 | 1.1077 | 4.2061 |
| 1.6616 | 8.7974 | 1.6616 | 6.6542 |
| 2.2155 | 12.169 | 2.2155 | 8.5812 |
| 2.7693 | 15.25 | 2.7693 | 10.082 |
| 3.3232 | 18.074 | 3.3232 | 11.253 |
| 3.877 | 20.677 | 3.877 | 12.172 |
| 4.4309 | 23.087 | 4.4309 | 12.897 |
| 4.9848 | 25.332 | 4.9848 | 13.472 |
| 5.5386 | 27.432 | 5.5386 | 13.93 |
| 6.0925 | 29.403 | 6.0925 | 14.297 |
| 6.6464 | 31.261 | 6.6464 | 14.591 |
| 7.2002 | 33.018 | 7.2002 | 14.828 |
| 7.7541 | 34.683 | 7.7541 | 15.019 |
| 8.3079 | 36.265 | 8.3079 | 15.174 |
| 8.8618 | 37.772 | 8.8618 | 15.299 |
| 9.4157 | 39.21 | 9.4157 | 15.401 |
| 9.9695 | 40.584 | 9.9695 | 15.484 |
| 10.5234 | 41.9 | 10.5234 | 15.552 |
| 11.0773 | 43.163 | 11.0773 | 15.607 |
| 11.6311 | 44.375 | 11.6311 | 15.653 |
| 12.185 | 45.54 | 12.185 | 15.69 |
| 12.7389 | 46.662 | 12.7389 | 15.72 |
| 13.2927 | 47.743 | 13.2927 | 15.745 |
| 13.8466 | 48.786 | 13.8466 | 15.765 |
| 14.4004 | 49.793 | 14.4004 | 15.782 |
| 14.9543 | 50.767 | 14.9543 | 15.796 |
| 15.5082 | 51.708 | 15.5082 | 15.808 |
| 16.062 | 52.619 | 16.062 | 15.817 |
| 16.6159 | 53.502 | 16.6159 | 15.825 |
| 17.1698 | 54.357 | 17.1698 | 15.831 |
| 17.7236 | 55.187 | 17.7236 | 15.837 |
| 18.2775 | 55.992 | 18.2775 | 15.841 |
| 18.8313 | 56.774 | 18.8313 | 15.845 |
| 19.3852 | 57.534 | 19.3852 | 15.848 |
| 19.9391 | 58.273 | 19.9391 | 15.85 |
| 20.4929 | 58.991 | 20.4929 | 15.852 |

**Figure 22** note: unlike figure 6M, these simulations assume linear partitioning for AC, log Kd = 8.76 (Jonker and Koelmans, 2002, ES&T 36, 3725-3734)

**CXTFIT**

| Bed Volumes | [ug/L] | Bed Volumes | [ug/L] | Bed Volumes | [ug/L] | Bed Volumes | [ug/L] | Bed Volumes | [ug/L] |
|---|---|---|---|---|---|---|---|---|---|
| 0.0538 | 0 | 0.0538 | 0 | 0.0538 | 0 | 0.0571 | 0 | 0.0571 | 0 |
| 0.5376 | 0 | 2.6882 | 0 | 2.6882 | 0 | 57142.8571 | 0 | 57.1429 | 0 |
| 1.0753 | 0 | 5.3763 | 0 | 5.3763 | 0 | 114285.7143 | 0 | 114.2857 | 0 |
| 1.6129 | 0 | 8.0645 | 0 | 8.0645 | 0 | 171428.5714 | 0 | 171.4286 | 0 |
| 2.1505 | 0 | 10.7527 | 0 | 10.7527 | 0 | 228571.4286 | 0 | 228.5714 | 0 |
| 2.6882 | 0 | 13.4409 | 0 | 13.4409 | 0 | 285714.2857 | 0 | 285.7143 | 0 |
| 3.2258 | 0 | 16.129 | 6.45E-12 | 16.129 | 0 | 342857.1429 | 0 | 342.8571 | 0 |
| 3.7634 | 0 | 18.8172 | 5.58E-09 | 18.8172 | 0 | 400000 | 0 | 400 | 0 |
| 4.3011 | 0 | 21.5054 | 7.90E-07 | 21.5054 | 0 | 457142.8571 | 0 | 457.1429 | 0 |
| 4.8387 | 0 | 24.1935 | 3.34E-05 | 24.1935 | 0 | 514285.7143 | 3.22E-13 | 514.2857 | 2.66E-13 |
| 5.3763 | 0 | 26.8817 | 6.09E-04 | 26.8817 | 0 | 571428.5714 | 5.20E-11 | 571.4286 | 4.36E-11 |
| 5.914 | 0 | 29.5699 | 6.01E-03 | 29.5699 | 0 | 628571.4286 | 3.16E-09 | 628.5714 | 2.69E-09 |
| 6.4516 | 5.55E-15 | 32.2581 | 0.0375 | 32.2581 | 0 | 685714.2857 | 9.20E-08 | 685.7143 | 7.97E-08 |
| 6.9892 | 5.33E-13 | 34.9462 | 0.1642 | 34.9462 | 0 | 742857.1429 | 1.52E-06 | 742.8571 | 1.34E-06 |
| 7.5269 | 1.94E-11 | 37.6344 | 0.5467 | 37.6344 | 0 | 800000 | 1.62E-05 | 800 | 1.44E-05 |
| 8.0645 | 4.27E-10 | 40.3226 | 1.462 | 40.3226 | 0 | 857142.8571 | 1.21E-04 | 857.1429 | 1.08E-04 |
| 8.6022 | 6.22E-09 | 43.0108 | 3.2769 | 43.0108 | 0 | 914285.7143 | 6.74E-04 | 914.2857 | 6.10E-04 |
| 9.1398 | 6.45E-08 | 45.6989 | 6.3606 | 45.6989 | 0 | 971428.5714 | 2.97E-03 | 971.4286 | 2.71E-03 |
| 9.6774 | 5.04E-07 | 48.3871 | 10.9689 | 48.3871 | 0 | 1028571.429 | 0.0107 | 1028.5714 | 9.88E-03 |
| 10.2151 | 3.10E-06 | 51.0753 | 17.1521 | 51.0753 | 0 | 1085714.286 | 0.0329 | 1085.7143 | 0.0305 |
| 10.7527 | 1.56E-05 | 53.7634 | 24.725 | 53.7634 | 2.22E-14 | 1142857.143 | 0.0877 | 1142.8571 | 0.0816 |
| 11.2903 | 6.59E-05 | 56.4516 | 33.3046 | 56.4516 | 3.22E-13 | 1200000 | 0.2069 | 1200 | 0.1937 |
| 11.828 | 2.40E-04 | 59.1398 | 42.3943 | 59.1398 | 3.25E-12 | 1257142.857 | 0.4403 | 1257.1429 | 0.4143 |
| 12.3656 | 7.65E-04 | 61.828 | 51.4809 | 61.828 | 2.67E-11 | 1314285.714 | 0.8565 | 1314.2857 | 0.8097 |
| 12.9032 | 2.18E-03 | 64.5161 | 60.1158 | 64.5161 | 1.82E-10 | 1371428.571 | 1.5408 | 1371.4286 | 1.4631 |
| 13.4409 | 5.62E-03 | 67.2043 | 67.9649 | 67.2043 | 1.06E-09 | 1428571.429 | 2.5883 | 1428.5714 | 2.4679 |
| 13.9785 | 0.0133 | 69.8925 | 74.8259 | 69.8925 | 5.29E-09 | 1485714.286 | 4.0941 | 1485.7143 | 3.9186 |
| 14.5161 | 0.0289 | 72.5806 | 80.6187 | 72.5806 | 2.33E-08 | 1542857.143 | 6.141 | 1542.8571 | 5.8988 |
| 15.0538 | 0.0588 | 75.2688 | 85.3609 | 75.2688 | 9.15E-08 | 1600000 | 8.7884 | 1600 | 8.4701 |
| 15.5914 | 0.1123 | 77.957 | 89.1376 | 77.957 | 3.24E-07 | 1657142.857 | 12.0635 | 1657.1429 | 11.663 |
| 16.129 | 0.2027 | 80.6452 | 92.0717 | 80.6452 | 1.05E-06 | 1714285.714 | 15.9564 | 1714.2857 | 15.4719 |
| 16.6667 | 0.3477 | 83.3333 | 94.301 | 83.3333 | 3.10E-06 | 1771428.571 | 20.4198 | 1771.4286 | 19.8542 |
| 17.2043 | 0.5698 | 86.0215 | 95.9611 | 86.0215 | 8.53E-06 | 1828571.429 | 25.3736 | 1828.5714 | 24.7342 |
| 17.7419 | 0.8956 | 88.7097 | 97.1749 | 88.7097 | 2.19E-05 | 1885714.286 | 30.7115 | 1885.7143 | 30.0096 |
| 18.2796 | 1.3555 | 91.3978 | 98.0478 | 91.3978 | 5.28E-05 | 1942857.143 | 36.3108 | 1942.8571 | 35.5605 |
| 18.8172 | 1.9821 | 94.086 | 98.6661 | 94.086 | 1.20E-04 | 2000000 | 42.0421 | 2000 | 41.2594 |
| 19.3548 | 2.8086 | 96.7742 | 99.0981 | 96.7742 | 2.59E-04 | 2057142.857 | 47.7782 | 2057.1429 | 46.9798 |
| 19.8925 | 3.8667 | 99.4624 | 99.3961 | 99.4624 | 5.33E-04 | 2114285.714 | 53.4024 | 2114.2857 | 52.6046 |
| 20.4301 | 5.1851 | 102.1505 | 99.5992 | 102.1505 | 1.05E-03 | 2171428.571 | 58.8136 | 2171.4286 | 58.0312 |
| 20.9677 | 6.7867 | 104.8387 | 99.7363 | 104.8387 | 1.98E-03 | 2228571.429 | 63.9298 | 2228.5714 | 63.1759 |
| 21.5054 | 8.6879 | 107.5269 | 99.8278 | 107.5269 | 3.60E-03 | 2285714.286 | 68.6901 | 2285.7143 | 67.9753 |
| 22.043 | 10.8965 | 110.2151 | 99.8884 | 110.2151 | 6.31E-03 | 2342857.143 | 73.0537 | 2342.8571 | 72.386 |
| 22.5806 | 13.4115 | 112.9032 | 99.9282 | 112.9032 | 0.0107 | 2400000 | 76.999 | 2400 | 76.3839 |
| 23.1183 | 16.2229 | 115.5914 | 99.9541 | 115.5914 | 0.0176 | 2457142.857 | 80.5206 | 2457.1429 | 79.9613 |
| 23.6559 | 19.3119 | 118.2796 | 99.9708 | 118.2796 | 0.0282 | 2514285.714 | 83.6268 | 2514.2857 | 83.1244 |
| 24.1935 | 22.6517 | 120.9677 | 99.9815 | 120.9677 | 0.044 | 2571428.571 | 86.3364 | 2571.4286 | 85.8901 |
| 24.7312 | 26.209 | 123.6559 | 99.9884 | 123.6559 | 0.0669 | 2628571.429 | 88.6757 | 2628.5714 | 88.2833 |
| 25.2688 | 29.9452 | 126.3441 | 99.9927 | 126.3441 | 0.0995 | 2685714.286 | 90.6759 | 2685.7143 | 90.3343 |
| 25.8065 | 33.8181 | 129.0323 | 99.9955 | 129.0323 | 0.1448 | 2742857.143 | 92.3706 | 2742.8571 | 92.076 |
| 26.3441 | 37.7834 | 131.7204 | 99.9972 | 131.7204 | 0.2064 | 2800000 | 93.7944 | 2800 | 93.5425 |
| 26.8817 | 41.7968 | 134.4086 | 99.9983 | 134.4086 | 0.2887 | 2857142.857 | 94.981 | 2857.1429 | 94.7675 |
| 27.4194 | 45.815 | 137.0968 | 99.9989 | 137.0968 | 0.3966 | 2914285.714 | 95.9627 | 2914.2857 | 95.783 |
| 27.957 | 49.7971 | 139.7849 | 99.9993 | 139.7849 | 0.5359 | 2971428.571 | 96.7691 | 2971.4286 | 96.6189 |
| 28.4946 | 53.7055 | 142.4731 | 99.9996 | 142.4731 | 0.7126 | 3028571.429 | 97.4271 | 3028.5714 | 97.3025 |
| 29.0323 | 57.5068 | 145.1613 | 99.9998 | 145.1613 | 0.9337 | 3085714.286 | 97.9607 | 3085.7143 | 97.858 |
| 29.5699 | 61.1726 | 147.8495 | 99.9999 | 147.8495 | 1.2062 | 3142857.143 | 98.3909 | 3142.8571 | 98.3067 |
| 30.1075 | 64.6789 | 150.5376 | 99.9999 | 150.5376 | 1.5377 | 3200000 | 98.7357 | 3200 | 98.6671 |
| 30.6452 | 68.0071 | 153.2258 | 99.9999 | 153.2258 | 1.9359 | 3257142.857 | 99.0107 | 3257.1429 | 98.9551 |
| 31.1828 | 71.1434 | 155.914 | 100 | 155.914 | 2.4083 | 3314285.714 | 99.2289 | 3314.2857 | 99.1841 |
| 31.7204 | 74.0786 | 158.6022 | 100 | 158.6022 | 2.9625 | 3371428.571 | 99.4012 | 3371.4286 | 99.3652 |
| 32.2581 | 76.8075 | 161.2903 | 100 | 161.2903 | 3.6057 | 3428571.429 | 99.5366 | 3428.5714 | 99.5079 |
| 32.7957 | 79.3291 | 163.9785 | 100 | 163.9785 | 4.3445 | 3485714.286 | 99.6427 | 3485.7143 | 99.6198 |
| 33.3333 | 81.6452 | 166.6667 | 100 | 166.6667 | 5.1847 | 3542857.143 | 99.7253 | 3542.8571 | 99.7073 |
| 33.871 | 83.7609 | 169.3548 | 100 | 169.3548 | 6.1315 | 3600000 | 99.7895 | 3600 | 99.7753 |
| 34.4086 | 85.683 | 172.043 | 100 | 172.043 | 7.189 | 3657142.857 | 99.8392 | 3657.1429 | 99.828 |
| 34.9462 | 87.4204 | 174.7312 | 100 | 174.7312 | 8.3601 | 3714285.714 | 99.8775 | 3714.2857 | 99.8687 |
| 35.4839 | 88.9833 | 177.4194 | 100 | 177.4194 | 9.6465 | 3771428.571 | 99.9069 | 3771.4286 | 99.9001 |
| 36.0215 | 90.3827 | 180.1075 | 100 | 180.1075 | 11.0489 | 3828571.429 | 99.9295 | 3828.5714 | 99.9242 |
| 36.5591 | 91.6302 | 182.7957 | 100 | 182.7957 | 12.5665 | 3885714.286 | 99.9467 | 3885.7143 | 99.9426 |
| 37.0968 | 92.7375 | 185.4839 | 100 | 185.4839 | 14.1971 | 3942857.143 | 99.9598 | 3942.8571 | 99.9566 |
| 37.6344 | 93.7164 | 188.172 | 100 | 188.172 | 15.9375 | 4000000 | 99.9698 | 4000 | 99.9673 |
| 38.172 | 94.5785 | 190.8602 | 100 | 190.8602 | 17.7832 | 4057142.857 | 99.9773 | 4057.1429 | 99.9754 |
| 38.7097 | 95.3349 | 193.5484 | 100 | 193.5484 | 19.7284 | 4114285.714 | 99.983 | 4114.2857 | 99.9816 |
| 39.2473 | 95.9962 | 196.2366 | 100 | 196.2366 | 21.7666 | 4171428.571 | 99.9873 | 4171.4286 | 99.9862 |
| 39.7849 | 96.5724 | 198.9247 | 100 | 198.9247 | 23.89 | 4228571.429 | 99.9905 | 4228.5714 | 99.9897 |
| 40.3226 | 97.0728 | 201.6129 | 100 | 201.6129 | 26.0902 | 4285714.286 | 99.9929 | 4285.7143 | 99.9923 |
| 40.8602 | 97.5061 | 204.3011 | 100 | 204.3011 | 28.3582 | 4342857.143 | 99.9948 | 4342.8571 | 99.9943 |
| 41.3978 | 97.88 | 206.9892 | 100 | 206.9892 | 30.6843 | 4400000 | 99.9961 | 4400 | 99.9957 |
| 41.9355 | 98.2019 | 209.6774 | 100 | 209.6774 | 33.0587 | 4457142.857 | 99.9971 | 4457.1429 | 99.9968 |
| 42.4731 | 98.4781 | 212.3656 | 100 | 212.3656 | 35.471 | 4514285.714 | 99.9979 | 4514.2857 | 99.9977 |
| 43.0108 | 98.7146 | 215.0538 | 100 | 215.0538 | 37.9111 | 4571428.571 | 99.9984 | 4571.4286 | 99.9983 |
| 43.5484 | 98.9165 | 217.7419 | 100 | 217.7419 | 40.3687 | 4628571.429 | 99.9988 | 4628.5714 | 99.9987 |
| 44.086 | 99.0884 | 220.4301 | 100 | 220.4301 | 42.8337 | 4685714.286 | 99.9991 | 4685.7143 | 99.9991 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 44.6237 | 99.2345 | 223.1183 | 100 | 223.1183 | 45.2965 | 4742857.143 | 99.9994 | 4742.8571 | 99.9993 |
| 45.1613 | 99.3584 | 225.8065 | 100 | 225.8065 | 47.7474 | 4800000 | 99.9995 | 4800 | 99.9995 |
| 45.6989 | 99.4631 | 228.4946 | 100 | 228.4946 | 50.1778 | 4857142.857 | 99.9997 | 4857.1429 | 99.9996 |
| 46.2366 | 99.5515 | 231.1828 | 100 | 231.1828 | 52.5791 | 4914285.714 | 99.9998 | 4914.2857 | 99.9997 |
| 46.7742 | 99.626 | 233.871 | 100 | 233.871 | 54.9436 | 4971428.571 | 99.9998 | 4971.4286 | 99.9998 |
| 47.3118 | 99.6886 | 236.5591 | 100 | 236.5591 | 57.2641 | 5028571.429 | 99.9999 | 5028.5714 | 99.9999 |
| 47.8495 | 99.7412 | 239.2473 | 100 | 239.2473 | 59.5342 | 5085714.286 | 99.9999 | 5085.7143 | 99.9999 |
| 48.3871 | 99.7851 | 241.9355 | 100 | 241.9355 | 61.7482 | 5142857.143 | 99.9999 | 5142.8571 | 99.9999 |
| 48.9247 | 99.8219 | 244.6237 | 100 | 244.6237 | 63.9009 | 5200000 | 99.9999 | 5200 | 99.9999 |
| 49.4624 | 99.8526 | 247.3118 | 100 | 247.3118 | 65.988 | 5257142.857 | 100 | 5257.1429 | 100 |
| 50 | 99.8782 | 250 | 100 | 250 | 68.006 | 5314285.714 | 100 | 5314.2857 | 100 |
| 50.5376 | 99.8994 | 252.6882 | 100 | 252.6882 | 69.9517 | 5371428.571 | 100 | 5371.4286 | 100 |
| 51.0753 | 99.9171 | 255.3763 | 100 | 255.3763 | 71.8229 | 5428571.429 | 100 | 5428.5714 | 100 |
| 51.6129 | 99.9317 | 258.0645 | 100 | 258.0645 | 73.6179 | 5485714.286 | 100 | 5485.7143 | 100 |
| 52.1505 | 99.9439 | 260.7527 | 100 | 260.7527 | 75.3356 | 5542857.143 | 100 | 5542.8571 | 100 |
| 52.6882 | 99.9539 | 263.4409 | 100 | 263.4409 | 76.9754 | 5600000 | 100 | 5600 | 100 |
| 53.2258 | 99.9622 | 266.129 | 100 | 266.129 | 78.5373 | 5657142.857 | 100 | 5657.1429 | 100 |
| 53.7634 | 99.969 | 268.8172 | 100 | 268.8172 | 80.0216 | 5714285.714 | 100 | 5714.2857 | 100 |
| 54.3011 | 99.9746 | 271.5054 | 100 | 271.5054 | 81.4291 | 5771428.571 | 100 | 5771.4286 | 100 |
| 54.8387 | 99.9793 | 274.1935 | 100 | 274.1935 | 82.761 | 5828571.429 | 100 | 5828.5714 | 100 |
| 55.3763 | 99.9831 | 276.8817 | 100 | 276.8817 | 84.0188 | 5885714.286 | 100 | 5885.7143 | 100 |
| 55.914 | 99.9862 | 279.5699 | 100 | 279.5699 | 85.2043 | 5942857.143 | 100 | 5942.8571 | 100 |
| 56.4516 | 99.9887 | 282.2581 | 100 | 282.2581 | 86.3194 | 6000000 | 100 | 6000 | 100 |
| 56.9892 | 99.9908 | 284.9462 | 100 | 284.9462 | 87.3665 | 6057142.857 | 100 | 6057.1429 | 100 |
| 57.5269 | 99.9925 | 287.6344 | 100 | 287.6344 | 88.3478 | 6114285.714 | 100 | 6114.2857 | 100 |
| 58.0645 | 99.9939 | 290.3226 | 100 | 290.3226 | 89.266 | 6171428.571 | 100 | 6171.4286 | 100 |
| 58.6022 | 99.9951 | 293.0108 | 100 | 293.0108 | 90.1235 | 6228571.429 | 100 | 6228.5714 | 100 |
| 59.1398 | 99.996 | 295.6989 | 100 | 295.6989 | 90.9231 | 6285714.286 | 100 | 6285.7143 | 100 |
| 59.6774 | 99.9968 | 298.3871 | 100 | 298.3871 | 91.6675 | 6342857.143 | 100 | 6342.8571 | 100 |
| 60.2151 | 99.9974 | 301.0753 | 100 | 301.0753 | 92.3594 | 6400000 | 100 | 6400 | 100 |
| 60.7527 | 99.9979 | 303.7634 | 100 | 303.7634 | 93.0015 | 6457142.857 | 100 | 6457.1429 | 100 |
| 61.2903 | 99.9983 | 306.4516 | 100 | 306.4516 | 93.5965 | 6514285.714 | 100 | 6514.2857 | 100 |
| 61.828 | 99.9986 | 309.1398 | 100 | 309.1398 | 94.147 | 6571428.571 | 100 | 6571.4286 | 100 |
| 62.3656 | 99.9989 | 311.828 | 100 | 311.828 | 94.6558 | 6628571.429 | 100 | 6628.5714 | 100 |
| 62.9032 | 99.9991 | 314.5161 | 100 | 314.5161 | 95.1252 | 6685714.286 | 100 | 6685.7143 | 100 |
| 63.4409 | 99.9993 | 317.2043 | 100 | 317.2043 | 95.5578 | 6742857.143 | 100 | 6742.8571 | 100 |
| 63.9785 | 99.9994 | 319.8925 | 100 | 319.8925 | 95.9559 | 6800000 | 100 | 6800 | 100 |
| 64.5161 | 99.9995 | 322.5806 | 100 | 322.5806 | 96.3218 | 6857142.857 | 100 | 6857.1429 | 100 |
| 65.0538 | 99.9996 | 325.2688 | 100 | 325.2688 | 96.6578 | 6914285.714 | 100 | 6914.2857 | 100 |
| 65.5914 | 99.9997 | 327.957 | 100 | 327.957 | 96.9658 | 6971428.571 | 100 | 6971.4286 | 100 |
| 66.129 | 99.9998 | 330.6452 | 100 | 330.6452 | 97.2478 | 7028571.429 | 100 | 7028.5714 | 100 |
| 66.6667 | 99.9998 | 333.3333 | 100 | 333.3333 | 97.5059 | 7085714.286 | 100 | 7085.7143 | 100 |
| 67.2043 | 99.9998 | 336.0215 | 100 | 336.0215 | 97.7417 | 7142857.143 | 100 | 7142.8571 | 100 |
| 67.7419 | 99.9999 | 338.7097 | 100 | 338.7097 | 97.9569 | 7200000 | 100 | 7200 | 100 |
| 68.2796 | 99.9999 | 341.3978 | 100 | 341.3978 | 98.1531 | 7257142.857 | 100 | 7257.1429 | 100 |
| 68.8172 | 99.9999 | 344.086 | 100 | 344.086 | 98.3318 | 7314285.714 | 100 | 7314.2857 | 100 |
| 69.3548 | 99.9999 | 346.7742 | 100 | 346.7742 | 98.4944 | 7371428.571 | 100 | 7371.4286 | 100 |
| 69.8925 | 99.9999 | 349.4624 | 100 | 349.4624 | 98.6422 | 7428571.429 | 100 | 7428.5714 | 100 |
| 70.4301 | 100 | 352.1505 | 100 | 352.1505 | 98.7764 | 7485714.286 | 100 | 7485.7143 | 100 |
| 70.9677 | 100 | 354.8387 | 100 | 354.8387 | 98.8982 | 7542857.143 | 100 | 7542.8571 | 100 |
| 71.5054 | 100 | 357.5269 | 100 | 357.5269 | 99.0086 | 7600000 | 100 | 7600 | 100 |
| 72.043 | 100 | 360.2151 | 100 | 360.2151 | 99.1086 | 7657142.857 | 100 | 7657.1429 | 100 |
| 72.5806 | 100 | 362.9032 | 100 | 362.9032 | 99.199 | 7714285.714 | 100 | 7714.2857 | 100 |
| 73.1183 | 100 | 365.5914 | 100 | 365.5914 | 99.2808 | 7771428.571 | 100 | 7771.4286 | 100 |
| 73.6559 | 100 | 368.2796 | 100 | 368.2796 | 99.3546 | 7828571.429 | 100 | 7828.5714 | 100 |
| 74.1935 | 100 | 370.9677 | 100 | 370.9677 | 99.4213 | 7885714.286 | 100 | 7885.7143 | 100 |
| 74.7312 | 100 | 373.6559 | 100 | 373.6559 | 99.4814 | 7942857.143 | 100 | 7942.8571 | 100 |
| 75.2688 | 100 | 376.3441 | 100 | 376.3441 | 99.5355 | 8000000 | 100 | 8000 | 100 |
| 75.8065 | 100 | 379.0323 | 100 | 379.0323 | 99.5843 | 8057142.857 | 100 | 8057.1429 | 100 |
| 76.3441 | 100 | 381.7204 | 100 | 381.7204 | 99.6282 | 8114285.714 | 100 | 8114.2857 | 100 |
| 76.8817 | 100 | 384.4086 | 100 | 384.4086 | 99.6676 | 8171428.571 | 100 | 8171.4286 | 100 |
| 77.4194 | 100 | 387.0968 | 100 | 387.0968 | 99.703 | 8228571.429 | 100 | 8228.5714 | 100 |
| 77.957 | 100 | 389.7849 | 100 | 389.7849 | 99.7349 | 8285714.286 | 100 | 8285.7143 | 100 |
| 78.4946 | 100 | 392.4731 | 100 | 392.4731 | 99.7634 | 8342857.143 | 100 | 8342.8571 | 100 |
| 79.0323 | 100 | 395.1613 | 100 | 395.1613 | 99.789 | 8400000 | 100 | 8400 | 100 |
| 79.5699 | 100 | 397.8495 | 100 | 397.8495 | 99.8119 | 8457142.857 | 100 | 8457.1429 | 100 |
| 80.1075 | 100 | 400.5376 | 100 | 400.5376 | 99.8324 | 8514285.714 | 100 | 8514.2857 | 100 |
| 80.6452 | 100 | 403.2258 | 100 | 403.2258 | 99.8508 | 8571428.571 | 100 | 8571.4286 | 100 |
| 81.1828 | 100 | 405.914 | 100 | 405.914 | 99.8672 | 8628571.429 | 100 | 8628.5714 | 100 |
| 81.7204 | 100 | 408.6022 | 100 | 408.6022 | 99.8819 | 8685714.286 | 100 | 8685.7143 | 100 |
| 82.2581 | 100 | 411.2903 | 100 | 411.2903 | 99.895 | 8742857.143 | 100 | 8742.8571 | 100 |
| 82.7957 | 100 | 413.9785 | 100 | 413.9785 | 99.9067 | 8800000 | 100 | 8800 | 100 |
| 83.3333 | 100 | 416.6667 | 100 | 416.6667 | 99.9171 | 8857142.857 | 100 | 8857.1429 | 100 |
| 83.871 | 100 | 419.3548 | 100 | 419.3548 | 99.9264 | 8914285.714 | 100 | 8914.2857 | 100 |
| 84.4086 | 100 | 422.043 | 100 | 422.043 | 99.9347 | 8971428.571 | 100 | 8971.4286 | 100 |
| 84.9462 | 100 | 424.7312 | 100 | 424.7312 | 99.9421 | 9028571.429 | 100 | 9028.5714 | 100 |
| 85.4839 | 100 | 427.4194 | 100 | 427.4194 | 99.9486 | 9085714.286 | 100 | 9085.7143 | 100 |
| 86.0215 | 100 | 430.1075 | 100 | 430.1075 | 99.9545 | 9142857.143 | 100 | 9142.8571 | 100 |
| 86.5591 | 100 | 432.7957 | 100 | 432.7957 | 99.9597 | 9200000 | 100 | 9200 | 100 |
| 87.0968 | 100 | 435.4839 | 100 | 435.4839 | 99.9643 | 9257142.857 | 100 | 9257.1429 | 100 |
| 87.6344 | 100 | 438.172 | 100 | 438.172 | 99.9684 | 9314285.714 | 100 | 9314.2857 | 100 |
| 88.172 | 100 | 440.8602 | 100 | 440.8602 | 99.972 | 9371428.571 | 100 | 9371.4286 | 100 |
| 88.7097 | 100 | 443.5484 | 100 | 443.5484 | 99.9753 | 9428571.429 | 100 | 9428.5714 | 100 |
| 89.2473 | 100 | 446.2366 | 100 | 446.2366 | 99.9781 | 9485714.286 | 100 | 9485.7143 | 100 |
| 89.7849 | 100 | 448.9247 | 100 | 448.9247 | 99.9807 | 9542857.143 | 100 | 9542.8571 | 100 |
| 90.3226 | 100 | 451.6129 | 100 | 451.6129 | 99.9829 | 9600000 | 100 | 9600 | 100 |
| 90.8602 | 100 | 454.3011 | 100 | 454.3011 | 99.9849 | 9657142.857 | 100 | 9657.1429 | 100 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 91.3978 | 100 | 456.9892 | 100 | 456.9892 | 99.9867 | 9714285.714 | 100 | 9714.2857 | 100 |
| 91.9355 | 100 | 459.6774 | 100 | 459.6774 | 99.9883 | 9771428.571 | 100 | 9771.4286 | 100 |
| 92.4731 | 100 | 462.3656 | 100 | 462.3656 | 99.9897 | 9828571.429 | 100 | 9828.5714 | 100 |
| 93.0108 | 100 | 465.0538 | 100 | 465.0538 | 99.9909 | 9885714.286 | 100 | 9885.7143 | 100 |
| 93.5484 | 100 | 467.7419 | 100 | 467.7419 | 99.992 | 9942857.143 | 100 | 9942.8571 | 100 |
| 94.086 | 100 | 470.4301 | 100 | 470.4301 | 99.9929 | 10000000 | 100 | 10000 | 100 |
| 94.6237 | 100 | 473.1183 | 100 | 473.1183 | 99.9938 | 10057142.86 | 100 | 10057.1429 | 100 |
| 95.1613 | 100 | 475.8065 | 100 | 475.8065 | 99.9945 | 10114285.71 | 100 | 10114.2857 | 100 |
| 95.6989 | 100 | 478.4946 | 100 | 478.4946 | 99.9952 | 10171428.57 | 100 | 10171.4286 | 100 |
| 96.2366 | 100 | 481.1828 | 100 | 481.1828 | 99.9957 | 10228571.43 | 100 | 10228.5714 | 100 |
| 96.7742 | 100 | 483.871 | 100 | 483.871 | 99.9963 | 10285714.29 | 100 | 10285.7143 | 100 |
| 97.3118 | 100 | 486.5591 | 100 | 486.5591 | 99.9967 | 10342857.14 | 100 | 10342.8571 | 100 |
| 97.8495 | 100 | 489.2473 | 100 | 489.2473 | 99.9971 | 10400000 | 100 | 10400 | 100 |
| 98.3871 | 100 | 491.9355 | 100 | 491.9355 | 99.9975 | 10457142.86 | 100 | 10457.1429 | 100 |
| 98.9247 | 100 | 494.6237 | 100 | 494.6237 | 99.9978 | 10514285.71 | 100 | 10514.2857 | 100 |
| 99.4624 | 100 | 497.3118 | 100 | 497.3118 | 99.998 | 10571428.57 | 100 | 10571.4286 | 100 |
| 100 | 100 | 500 | 100 | 500 | 99.9983 | 10628571.43 | 100 | 10628.5714 | 100 |
| 100.5376 | 100 | 502.6882 | 100 | 502.6882 | 99.9985 | 10685714.29 | 100 | 10685.7143 | 100 |
| 101.0753 | 100 | 505.3763 | 100 | 505.3763 | 99.9987 | 10742857.14 | 100 | 10742.8571 | 100 |
| 101.6129 | 100 | 508.0645 | 100 | 508.0645 | 99.9988 | 10800000 | 100 | 10800 | 100 |
| 102.1505 | 100 | 510.7527 | 100 | 510.7527 | 99.999 | 10857142.86 | 100 | 10857.1429 | 100 |
| 102.6882 | 100 | 513.4409 | 100 | 513.4409 | 99.9991 | 10914285.71 | 100 | 10914.2857 | 100 |
| 103.2258 | 100 | 516.129 | 100 | 516.129 | 99.9992 | 10971428.57 | 100 | 10971.4286 | 100 |
| 103.7634 | 100 | 518.8172 | 100 | 518.8172 | 99.9993 | 11028571.43 | 100 | 11028.5714 | 100 |
| 104.3011 | 100 | 521.5054 | 100 | 521.5054 | 99.9994 | 11085714.29 | 100 | 11085.7143 | 100 |
| 104.8387 | 100 | 524.1935 | 100 | 524.1935 | 99.9995 | 11142857.14 | 100 | 11142.8571 | 100 |
| 105.3763 | 100 | 526.8817 | 100 | 526.8817 | 99.9995 | 11200000 | 100 | 11200 | 100 |
| 105.914 | 100 | 529.5699 | 100 | 529.5699 | 99.9996 | 11257142.86 | 100 | 11257.1429 | 100 |
| 106.4516 | 100 | 532.2581 | 100 | 532.2581 | 99.9996 | 11314285.71 | 100 | 11314.2857 | 100 |
| 106.9892 | 100 | 534.9462 | 100 | 534.9462 | 99.9997 | 11371428.57 | 100 | 11371.4286 | 100 |
| 107.5269 | 100 | 537.6344 | 100 | 537.6344 | 99.9997 | 11428571.43 | 100 | 11428.5714 | 100 |
| 108.0645 | 100 | 540.3226 | 100 | 540.3226 | 99.9998 | 11485714.29 | 100 | 11485.7143 | 100 |
| 108.6022 | 100 | 543.0108 | 100 | 543.0108 | 99.9998 | 11542857.14 | 100 | 11542.8571 | 100 |
| 109.1398 | 100 | 545.6989 | 100 | 545.6989 | 99.9998 | 11600000 | 100 | 11600 | 100 |
| 109.6774 | 100 | 548.3871 | 100 | 548.3871 | 99.9998 | 11657142.86 | 100 | 11657.1429 | 100 |
| 110.2151 | 100 | 551.0753 | 100 | 551.0753 | 99.9999 | 11714285.71 | 100 | 11714.2857 | 100 |
| 110.7527 | 100 | 553.7634 | 100 | 553.7634 | 99.9999 | 11771428.57 | 100 | 11771.4286 | 100 |
| 111.2903 | 100 | 556.4516 | 100 | 556.4516 | 99.9999 | 11828571.43 | 100 | 11828.5714 | 100 |
| 111.828 | 100 | 559.1398 | 100 | 559.1398 | 99.9999 | 11885714.29 | 100 | 11885.7143 | 100 |
| 112.3656 | 100 | 561.828 | 100 | 561.828 | 99.9999 | 11942857.14 | 100 | 11942.8571 | 100 |
| 112.9032 | 100 | 564.5161 | 100 | 564.5161 | 99.9999 | 12000000 | 100 | 12000 | 100 |
| 113.4409 | 100 | 567.2043 | 100 | 567.2043 | 99.9999 | 12057142.86 | 100 | 12057.1429 | 100 |
| 113.9785 | 100 | 569.8925 | 100 | 569.8925 | 99.9999 | 12114285.71 | 100 | 12114.2857 | 100 |
| 114.5161 | 100 | 572.5806 | 100 | 572.5806 | 100 | 12171428.57 | 100 | 12171.4286 | 100 |
| 115.0538 | 100 | 575.2688 | 100 | 575.2688 | 100 | 12228571.43 | 100 | 12228.5714 | 100 |
| 115.5914 | 100 | 577.957 | 100 | 577.957 | 100 | 12285714.29 | 100 | 12285.7143 | 100 |
| 116.129 | 100 | 580.6452 | 100 | 580.6452 | 100 | 12342857.14 | 100 | 12342.8571 | 100 |
| 116.6667 | 100 | 583.3333 | 100 | 583.3333 | 100 | 12400000 | 100 | 12400 | 100 |
| 117.2043 | 100 | 586.0215 | 100 | 586.0215 | 100 | 12457142.86 | 100 | 12457.1429 | 100 |
| 117.7419 | 100 | 588.7097 | 100 | 588.7097 | 100 | 12514285.71 | 100 | 12514.2857 | 100 |
| 118.2796 | 100 | 591.3978 | 100 | 591.3978 | 100 | 12571428.57 | 100 | 12571.4286 | 100 |
| 118.8172 | 100 | 594.086 | 100 | 594.086 | 100 | 12628571.43 | 100 | 12628.5714 | 100 |
| 119.3548 | 100 | 596.7742 | 100 | 596.7742 | 100 | 12685714.29 | 100 | 12685.7143 | 100 |
| 119.8925 | 100 | 599.4624 | 100 | 599.4624 | 100 | 12742857.14 | 100 | 12742.8571 | 100 |
| 120.4301 | 100 | 602.1505 | 100 | 602.1505 | 100 | 12800000 | 100 | 12800 | 100 |
| 120.9677 | 100 | 604.8387 | 100 | 604.8387 | 100 | 12857142.86 | 100 | 12857.1429 | 100 |
| 121.5054 | 100 | 607.5269 | 100 | 607.5269 | 100 | 12914285.71 | 100 | 12914.2857 | 100 |
| 122.043 | 100 | 610.2151 | 100 | 610.2151 | 100 | 12971428.57 | 100 | 12971.4286 | 100 |
| 122.5806 | 100 | 612.9032 | 100 | 612.9032 | 100 | 13028571.43 | 100 | 13028.5714 | 100 |
| 123.1183 | 100 | 615.5914 | 100 | 615.5914 | 100 | 13085714.29 | 100 | 13085.7143 | 100 |
| 123.6559 | 100 | 618.2796 | 100 | 618.2796 | 100 | 13142857.14 | 100 | 13142.8571 | 100 |
| 124.1935 | 100 | 620.9677 | 100 | 620.9677 | 100 | 13200000 | 100 | 13200 | 100 |
| 124.7312 | 100 | 623.6559 | 100 | 623.6559 | 100 | 13257142.86 | 100 | 13257.1429 | 100 |
| 125.2688 | 100 | 626.3441 | 100 | 626.3441 | 100 | 13314285.71 | 100 | 13314.2857 | 100 |
| 125.8065 | 100 | 629.0323 | 100 | 629.0323 | 100 | 13371428.57 | 100 | 13371.4286 | 100 |
| 126.3441 | 100 | 631.7204 | 100 | 631.7204 | 100 | 13428571.43 | 100 | 13428.5714 | 100 |
| 126.8817 | 100 | 634.4086 | 100 | 634.4086 | 100 | 13485714.29 | 100 | 13485.7143 | 100 |
| 127.4194 | 100 | 637.0968 | 100 | 637.0968 | 100 | 13542857.14 | 100 | 13542.8571 | 100 |
| 127.957 | 100 | 639.7849 | 100 | 639.7849 | 100 | 13600000 | 100 | 13600 | 100 |
| 128.4946 | 100 | 642.4731 | 100 | 642.4731 | 100 | 13657142.86 | 100 | 13657.1429 | 100 |
| 129.0323 | 100 | 645.1613 | 100 | 645.1613 | 100 | 13714285.71 | 100 | 13714.2857 | 100 |
| 129.5699 | 100 | 647.8495 | 100 | 647.8495 | 100 | 13771428.57 | 100 | 13771.4286 | 100 |
| 130.1075 | 100 | 650.5376 | 100 | 650.5376 | 100 | 13828571.43 | 100 | 13828.5714 | 100 |
| 130.6452 | 100 | 653.2258 | 100 | 653.2258 | 100 | 13885714.29 | 100 | 13885.7143 | 100 |
| 131.1828 | 100 | 655.914 | 100 | 655.914 | 100 | 13942857.14 | 100 | 13942.8571 | 100 |
| 131.7204 | 100 | 658.6022 | 100 | 658.6022 | 100 | 14000000 | 100 | 14000 | 100 |
| 132.2581 | 100 | 661.2903 | 100 | 661.2903 | 100 | 14057142.86 | 100 | 14057.1429 | 100 |
| 132.7957 | 100 | 663.9785 | 100 | 663.9785 | 100 | 14114285.71 | 100 | 14114.2857 | 100 |
| 133.3333 | 100 | 666.6667 | 100 | 666.6667 | 100 | 14171428.57 | 100 | 14171.4286 | 100 |
| 133.871 | 100 | 669.3548 | 100 | 669.3548 | 100 | 14228571.43 | 100 | 14228.5714 | 100 |
| 134.4086 | 100 | 672.043 | 100 | 672.043 | 100 | 14285714.29 | 100 | 14285.7143 | 100 |
| 134.9462 | 100 | 674.7312 | 100 | 674.7312 | 100 | 14342857.14 | 100 | 14342.8571 | 100 |
| 135.4839 | 100 | 677.4194 | 100 | 677.4194 | 100 | 14400000 | 100 | 14400 | 100 |
| 136.0215 | 100 | 680.1075 | 100 | 680.1075 | 100 | 14457142.86 | 100 | 14457.1429 | 100 |
| 136.5591 | 100 | 682.7957 | 100 | 682.7957 | 100 | 14514285.71 | 100 | 14514.2857 | 100 |
| 137.0968 | 100 | 685.4839 | 100 | 685.4839 | 100 | 14571428.57 | 100 | 14571.4286 | 100 |
| 47430000 | 100 | 47430000 | 100 | 47430000 | 100 | 44625000 | 100 | 44625000 | 100 |

**MODEL PARAMETERS**

| | Cap with: No Amendment | std error[+] | Cap with: 0.2% TOC Amendment | std error[+] | Cap with: 2% GAC Amendment |
|---|---|---|---|---|---|
| Bulk Density, kg/L | 1.6 | | 1.13 | | 1.65 |
| Effective Porosity | 0.28 | 0.001 | 0.26 | 0.0007 | 0.28 |
| longitudinal dispersivity, cm | 1.65 | 0.09 | 1.08 | 0.04 | 1.65 |
| flux, Darcy velocity, cm/day | 31 | | 32 | | 32 |
| Kd Phenanthrene, L/kg | 4.73 | | 22.23 | | |
| Kd Pyrene, L/kg | 24 | | 162.4 | | |
| Kfr Phenanthrene, $(mg/Kg)/(mg/L)^{1/n}$ | | | | | 53703.2 |
| n, Phenanthrene | | | | | 0.41 |